

Hot Electrons in Germanium and Ohm's Law

By W. SHOCKLEY

The data of E. J. Ryder on the mobility of electrons in electric fields up to 40,000 volts per cm are analyzed. The mobility decreases many fold due to the influence of scattering by optical modes and due to increases of electron energy. It is estimated that electron "temperatures" as high as 4000°K have been produced in specimens having temperatures of atomic vibration of 300° K. The critical drift velocity above which there are deviations from Ohm's law is about 2.6×10^6 cm/sec. This is three times higher than the elementary theory and an explanation in terms of complex energy surfaces is proposed.

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1. INTRODUCTION: FUNDAMENTAL DEVIATIONS FROM OHM'S LAW

THE starting point of many branches of physics is a linear relation. Among the most prominent of these are Hooke's law, which relates stress and strain for solid bodies, Newton's second law of motion $F = ma$ and Ohm's law. In all of these cases, the linear relation is only an approximation that may be regarded as the first term in a Taylor's expansion of the functional relationship between the two variables. Important physical principles are brought to attention when the nonlinear range is reached.

Of the three laws mentioned, Newton's is, of course, the one in which the failure of linearity is the most significant representing as it does the entrance of relativistic effects into the laws of motion.

The failure of Hooke's law may be of either a primary or secondary form.

If a solid contains voids, then under a certain pressure it will crumble and fill the voids. This is a secondary effect. If the sample is homogeneous, however, high pressures will produce fundamental deviations from Hooke's law, these deviations arising from the nonlinearity of the forces between atoms. Studies of these nonlinear effects by Bridgman have, among other things, put on a firmer basis the understanding of the forces between ions in ionic crystals and the pressures of electron gases in metals.

Deviations from Ohm's law for electronic conduction in semiconductors are almost the rule rather than the exception, but the most familiar cases are secondary rather than primary. The primary linear relation for the conduction process is that between the drift velocity of an electron, or hole, and the electric field that drives it. This relationship is

$$v_d = \mu_0(T) E, \quad (1.1)$$

where the mobility $\mu_0(T)$ is a function of the temperature T of the specimen. By a *fundamental deviation from Ohm's law* we shall mean a deviation in this linear relationship arising from the largeness of E rather than other causes.

Thermistor action is typical of a secondary deviation from Ohm's law. A thermistor is usually a two-terminal circuit element in which the current flows through an electronic semiconductor. The semiconductor has the property that its resistance decreases rapidly as the temperature increases; and the physical basis for this decrease is an increase in the number of conducting electrons (or holes or both) with increasing temperature. The passage of current heats the thermistor and its resistance changes; consequently the linear relation between current and voltage fails and in fact there may result a decrease of voltage with increasing current so that a differential negative resistance is observed. The electric fields are so low, however, that equation (1.1) is valid provided the dependence of μ_0 on the temperature is taken into account. An experimental proof that no fundamental deviation of Ohm's law occurs is furnished by applying a small a-c. test signal on top of a d-c. bias that produces heating. If the frequency is much higher than the thermal relaxation rate, the a-c. resistance is found to be simply that expected for the observed temperature.

The principal nonlinearities of crystal rectifiers, or varistors, and of transistors are also secondary and are associated with changing numbers of current carriers.

In this article we shall discuss some experimental evidence of fundamental deviations in Ohm's law for electrons in n -type germanium obtained by E. J. Ryder of Bell Telephone Laboratories.¹ We shall describe his ex-

¹ E. J. Ryder and W. Shockley, *Phys. Rev.* **81**, 139 (1951).

perimental techniques and results briefly in the next section and shall then present some aspects of the quantitative theory that explains them, leaving the bulk of the mathematical manipulations for the appendices.

Before discussing Ryder's results, we may indicate why his procedure succeeded whereas previous attempts, of which there have apparently been a number, largely unpublished, have failed. Ryder's work takes advantage of three factors: (1) the availability of electrical pulses of microsecond duration, (2) the high resistivity of germanium, and (3) the high mobility of electrons in germanium. Because of (3), it is possible to deliver energy to electrons at relatively high rates by electric fields. In effect this "heats" the electrons above the temperature of the crystal and lowers their mobility. The generalized equation is then

$$v_d = \mu(T, E)E \quad (1.2)$$

where the fact that μ depends on E represents the fundamental nonlinearity. We shall show that Ryder's techniques raise the "temperature" of the electrons by a factor of about thirteen fold to above 4000°K. Since the resistivity is high, say 10 ohm cm, the power delivered to the specimen is sufficiently low that the heating in one pulse is negligible. The pulse repetition rate is then kept so low that accumulated heat is negligible also.

These conditions are enormously more favorable than those met with in metals. In a metal the average electron energy is several electron volts; in order to double this energy, each electron would acquire an added energy roughly equal to the cohesive energy per atom of the crystal. Furthermore, in a metal there is about one conduction electron per atom, compared with 10^{-7} per atom in Ryder's samples. Thus the stored energy due to "hot" electrons in a metal would be enough to vaporize it, whereas in germanium, or a similar semiconductor, a temperature of 10,000°K for the electrons would be enough to raise the crystal less than 0.01°K. From this reasoning it appears that it will be extremely difficult, if not impossible, to produce significant fundamental deviations from Ohm's law in metals and certainly impossible to produce effects of the magnitude described below.

It should be pointed out that the behavior of electrons in crystals in fields so high that equation (1) fails have been subject to both experimental and theoretical investigation in connection with dielectric breakdown.² The work does not apply to cases in which the specimens obey Ohm's law at low fields, however, and the experiments do not permit accurate deter-

² See, for example, H. Fröhlich and F. Seitz, *Phys. Rev.* 79, 526 (1950) and F. Seitz *Phys. Rev.* 76, 1376 (1950). Much of the treatment presented in the Appendices is essentially equivalent to that given in Seitz. In our Appendices, however, we give much more emphasis to the low field case. The Seitz paper also contains a review of the literature to which the reader is referred.

minations of v_d as a function of E . From the theoretical side also the emphasis has been on fields so high that the linear range is neglected so that the transition from linear to nonlinear is not stressed.

The current theories of dielectric breakdown are based on the principle of "secondary generation" or "electron multiplication." Thus if an electron acquires enough energy from the electric field, it will be capable of producing secondaries by collision with bound electrons, and the repetition of this process will lead to an avalanche. Our theory indicates that in germanium, even at fields as high as 200,000 volts/cm, few electrons will have enough energy to produce secondaries. At about those fields, however, another phenomenon occurs.

In 1934 C. Zener³ proposed that dielectric breakdown was due to a primary effect: the field induced generation of hole-electron pairs. His mathematical theory is similar to that for field emission from cold metal points and to that for radioactive decay. It involves the "tunnelling" of electrons through regions in which their wave functions are attenuated, rather than running, waves.

Zener's theory does not seem to apply to breakdown; however, it does apply to the high electric fields produced in rectifying p - n junctions in germanium when these are biased in the reverse direction. Under these conditions fields of the order of 200,000 volts/cm are produced. The mobilities of electrons, or holes, in these fields have not been measured. It has been shown,⁴ however, that secondary production is very small. At these fields a sort of "breakdown" effect occurs and above a critical value of the voltage a very rapid increase in current is observed. This current appears to be of the nature predicted by Zener. It is stable at a given voltage, has a small temperature coefficient and will probably be useful in semiconductor analogues of "voltage regulator tubes" and protective devices.

As is shown in the treatment given in qualitative terms in Section 3 and in more detail in the Appendices, the explanation of the fundamental deviations from Ohm's law is based on the theory of electron waves. The investigations described in this paper may thus be regarded as furnishing evidence for the wave nature of conduction electrons in germanium and are thus related to the researches of C. J. Davisson, to whom this volume is dedicated, and his collaborator, L. H. Germer. The Davisson-Germer experiments were concerned chiefly with electron waves in free space and with high energy electrons in crystals. Both of these cases are simpler than that dealt with in this paper. Electrons in the conduction band in germanium appear to behave as though they were in a multiply refracting medium in which they may have

³ C. Zener, *Proc. Roy. Soc.* 145, 523 (1934).

⁴ K. C. McAfee, E. J. Ryder, W. Shockley and M. Sparks, *Phys. Rev.* 83, 650 (1951).

several velocities of propagation for any specified direction of propagation and frequency. It is to be hoped that more detailed analyses of the data obtained by Ryder, together with quantitative interpretations of certain observations of magnetoresistance, may lead to a unique evaluation of the "refractive constants" of the medium for the electron waves; this possibility is discussed briefly in Section 5. The phenomena in the Zener current range afford another new opportunity to study electron waves in crystals. The waves involved in this effect are those with energies in the energy gap between the conduction band and the valence band; waves in this range have received little attention from either the experimental or theoretical side.

2. E. J. RYDER'S RESULTS

One of germanium's most noted attributes is its ability to give amplification of electrical signals when made into a transistor. The basic phenomenon for many types of transistors is that of "carrier injection." As is

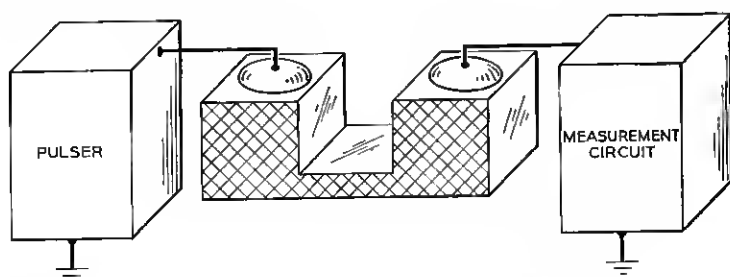


Fig. 1—The principles of E. J. Ryder's technique for observing conductivity in high electric fields.

well known, germanium may carry current either by the electron mechanism in which case it is called *n*-type germanium, or by the mechanism of hole conduction in which case it is called *p*-type. If a suitably prepared electrode is placed on an *n*-type specimen and current is caused to flow in the sense that removes electrons from the specimen, then the process may cause "hole injection." In this case in addition to removing conduction electrons from the germanium, electrons are removed from the valence bonds so that holes are injected. This leads to nonlinear effects because, as the current passes through the specimen, the number of carriers in the specimen changes and so does its resistivity.

In order to avoid the secondary deviations from Ohm's law due to carrier injection, Ryder has designed specimens of the form shown in Fig. 1. These specimens have large ends to which the metal electrodes are attached. The resistance arises chiefly from a thin section of the material connecting the

large ends. Since the fields at the large ends are small, carrier injection is largely suppressed; furthermore, the electric fields are applied for such a short time during the pulse that, even if holes were injected at one of the ends, they would not have time to reach the narrow section of the bridge and modulate its conductivity during the period of the pulse.

Further causes of non-linearity can arise from inhomogeneities in the germanium material itself. For example grain boundaries in polycrystalline germanium are known to have added electrical resistance. Difficulties due

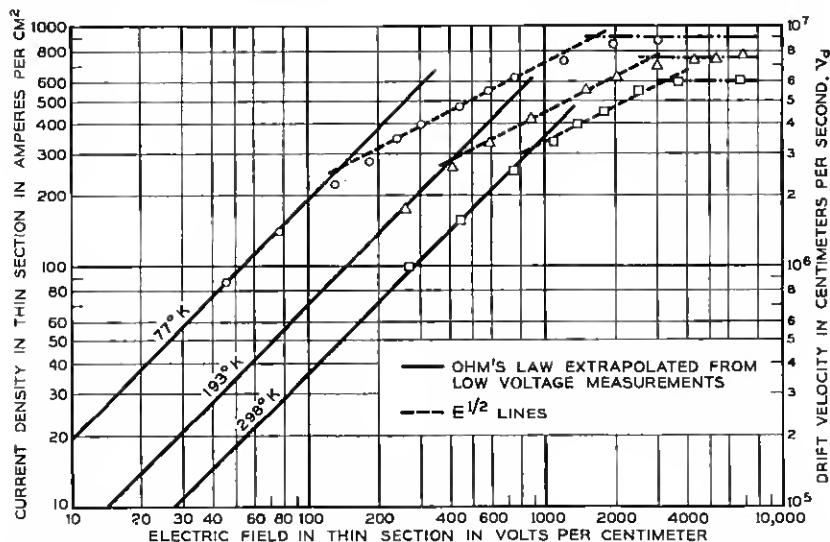


Fig. 2—Currents and estimated drift velocities deduced from E. J. Ryder's pulse data on a specimen of *n*-type germanium of 2.7 ohm-cm resistivity. [The fact that the numerical values of current density and drift velocity have the same digits is a consequence of the accident that $\sigma = 1/2.7 = 0.37$ is almost exactly 10^{-4} times the mobility.]

to inhomogeneity have largely been eliminated in these experiments by the use of highly homogeneous single-crystal germanium material furnished by G. K. Teal and his collaborators.

Other experimental precautions are necessary, such as assuring a smooth polished surface on the filament; if this is not done, apparently holes are injected from the surface irregularities of the thin section between the large ends. It is also necessary to make corrections for end effects since some of the resistance arises within the large blocks themselves.

Some of the data obtained by Ryder are shown in Fig. 2. The drift velocity, plotted as ordinate, is not measured directly but is inferred from the measured currents through the specimen by the following reasoning:

In a specimen at room temperature the drift velocity of electrons is given by the equation

$$v_d = 3600 E \text{ cm/sec} \quad (2.1)$$

when E is expressed in volts per cm.⁵ At 100 volts per cm, for example, (which is below the non-linear range) the velocity of electrons should be 3.6×10^5 . This establishes the drift velocity scale for room temperature. From other measurements of the germanium specimen of Fig. 2, it is concluded that the number of electrons available for conduction is substantially independent of temperature down to liquid air temperatures. Consequently, for this temperature range the drift velocity should be directly proportional to the current in the specimen. The other two sets of data are accordingly simply scaled in proportion to their currents.

On the figure we also show extrapolated lines at 45 degrees corresponding to Ohm's law. From these we see that decreases in mobility of tenfold or more have been produced in these experiments for high field conditions.

The data for each temperature fall approximately on three lines: The low field or Ohm's law region, an intermediate region over which v_d is proportional to $E^{1/2}$ and μ is proportional to $E^{-1/2}$, and a saturation region. The break at low fields comes at drift velocity of about 3×10^6 cm/sec for all three cases. This break, according to theory, should come when the drift velocity is several times the speed of sound in germanium, the speed of sound being about 5.4×10^5 cm/sec. The limiting drift velocity at higher fields is associated with the energy required to excite a particular type of atomic vibration, called an "optical mode." It comes at approximately the value of drift velocity predicted by theory.⁶ The theoretical curves, computed in the appendices, do not break into the sharp line section suggested on Fig. 2. However, they show the distinct influences of separate causes and fit the data reasonably well, as we shall show below in connection with Fig. 5.

3. THEORY OF DEVIATIONS FROM OHM'S LAW

3a. Electrons in *n*-Type Germanium⁷

The specimens we shall consider are of *n*-type germanium and have resistivities of several ohm cm. The conductivity arises from the presence

⁵ J. R. Haynes and W. Shockley, *Phys. Rev.* 81, 835 (1951).

⁶ The observation and explanation of these general features was presented in our first publications: E. J. Ryder and W. Shockley *Phys. Rev.* 81, 139 (1951) and 82, 330 (1951).

⁷ The material under this heading is treated in more detail in the author's book, "Electrons and Holes in Semiconductors," D. van Nostrand (1950), Chapter I. This book will be referred to subsequently as *E and H in S*.

of donors: chemical impurities such as arsenic or antimony. These donors substitute themselves for germanium atoms in the crystal structure, form electron-pair bonds with their four neighbors and release their fifth valence electron to the conduction band. The density of donors is about $10^{15}/\text{cm}^3$ or one per cube $10^{-3} \text{ cm} = 1000 \text{ \AA}$ on an edge. The donors are fixed positive charges and do not move in electric fields. Their charges neutralize those of the electrons. The electrostatic energy of interaction between electrons and donors leads to a deflection of the electron's motion. For the temperatures of Fig. 2, however, this effect is unimportant compared to the effect of thermal vibrations of the atoms.

The electrons in the conduction band move in accordance with a wave equation. They may, however, be thought of as particles. The justification is that, under many experimental conditions, the wave functions will actually be wave packets. These wave packets, it can be shown, behave much as particles and can be dealt with as particles, at least provided the phenomena considered do not involve distances smaller than the size of the wave packet.

Under conditions of thermal equilibrium we may think of the 10^{15} electrons in each cubic centimeter as an electron gas with the electrons (as wave packets) moving at random with an average kinetic energy of motion of $(3/2)kT$.

If the atoms of the crystal were held rigidly at rest in a perfectly regular crystal structure, an electron wave, and a wave packet too, would be transmitted through it with no scattering. At 300°K the vibrations are such that the wave packet moves for only 2500 \AA before being scattered. At low temperatures, the mean free path is longer and at liquid hydrogen temperatures it is so long that thermal vibrations are less important than the fields of the ionized donors. As stated above, however, we may neglect this scattering by ions over the temperature range of Fig. 2.

Before proceeding with the discussion of the interactions of electrons and thermal vibration we shall point out that two problems must be solved before the dependence of mobility upon electric field can be explained:

First, the mechanisms of the individual processes must be analyzed. This is the basic physical problem. In order to solve it we must apply quantum mechanics to the model representing the electron moving in the crystal and determine the probabilities of various types of transitions and some appropriate averages.

Second, the statistical consequences must be worked out. On the basis of the individual processes, the statistics of the assemblage of electrons must be analyzed and a steady state solution found.

The first problem poses the more physical problems and is given the most

attention. The second problem is more difficult mathematically. It is given only an approximate treatment which is adequate, however, to indicate that the solution to the first problem contains the necessary features to explain the experiments.

3b. *The Phonons*

We must next consider how to describe the thermal vibrations and to evaluate their interactions with the electrons. We shall present only the principal results of the mathematical analysis here, leaving the details for the appendices. The earliest treatment of thermal vibration in a crystal was that of Einstein, who considered each atom to be a separate harmonic oscillator. This model was improved on by Debye who treated the crystal as an elastic continuum that could support running waves. Debye's method is regarded as essentially correct and we, therefore, resolve the atomic motions into a set of running waves, or normal modes. There are three times as many independent normal modes as there are atoms in the crystal, or one per degree of freedom, and any possible atomic motion of the crystal may be made up as a sort of Fourier series in these normal modes.

Each normal mode must be treated as a Planck oscillator and has a system of energy levels with values

$$(n + 1/2)h\nu \quad (3.1)$$

where ν is its frequency of vibration. Each quantum of energy is referred to as a *phonon*; if a normal mode makes a transition with $\delta n = +1$, we say a phonon has been emitted and if $\delta n = -1$, we say one has been absorbed.

The description of the crystal in terms of phonons is in close analogy with the description of electromagnetic waves in a cavity in terms of *photons*. For the case of light, the electromagnetic state of the cavity is determined by finding the normal modes, which are treated as quantized oscillators, and transitions with $\delta n = \pm 1$ correspond to photon emission and absorption.

The normal modes for the crystal are unlike those for light. For low frequencies the waves are essentially the microscopic transverse and longitudinal waves of a solid. As the wave length becomes shorter, however, the sound velocity varies and there is a limiting minimum wave length which is about twice the spacing between atoms. In order to understand the energy losses of electrons in high fields, we must consider the role of this minimum wave length. For this purpose we shall describe the dependence of frequency upon wave length for a longitudinal mode.

Accordingly we consider the frequency of the normal modes corresponding to a longitudinal wave propagating along a cube axis. Rather than

using the wave length λ as a variable, we use the wave number or $(1/\lambda)$. For long waves the frequency is simply

$$\nu = c/\lambda = c(1/\lambda). \quad (3.2)$$

This corresponds to the straight line portion for low frequencies in Fig. 3. This portion extends to a wave length equal to twice the lattice constant a of the crystal.

Figure 3 shows another curve which has a high frequency even for $(1/\lambda) = 0$ or infinite wave length. The presence of this branch of the "vibrational spectrum" is due to the fact that the diamond structure has two

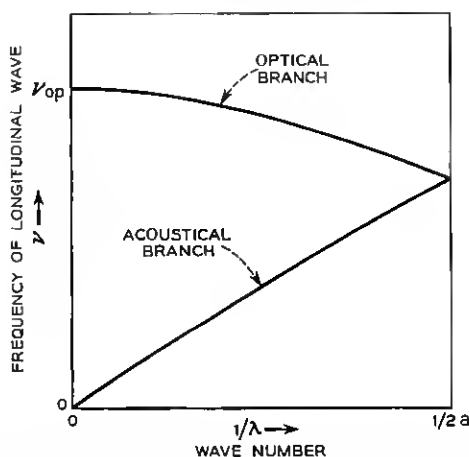


Fig. 3—Frequency of longitudinal vibrations in [100] direction in the diamond structure. (In this particular direction of propagation the acoustical and optical branches join smoothly at the same frequency; for other directions, there is a discontinuity in frequency. The dependence of ν upon $1/\lambda$ is approximated by a sine wave.)

atoms per unit cell. (The diamond structure is made of two face centered cubic arrays of atoms, juxtaposed so that each atom of one array is centrally situated in respect to a tetrahedron of four atoms of the other array, with which it forms four electron-pair bonds. The unit cell contains one atom of each array.) As a consequence of this it is possible to have a vibration in which one atom vibrates in the plus x direction while the other atom vibrates oppositely and to have this same motion occur in phase in every unit cell. Such a vibration is considered to have infinite wave length, since every unit cell does the same thing at the same time. It has the highest possible frequency since the pattern of motion involves directly opposed motions of nearest neighbors. If the motion is modified so as to have dif-

ferent phases in adjoining unit cells, and thus to correspond to a finite wave length, the frequency drops.

The opposed motions are referred to as "optical modes" by analogy with polar crystals. In a crystal of sodium chloride there is one Cl^- and one Na^+ per unit cell. In the opposed type of motion, ions of like sign move one way and opposite to those of the other sign. This relative motion of charge polarizes the crystal and phonons of this type of vibration can absorb or emit light. Because of this optical activity the mode is termed optical.

The name "optical" is carried over to valence crystals to describe the opposed form of motion, although no polarization accompanies the displacement in the latter case.

3c. The Selection Rules

We shall next consider the laws which govern the interchange of energy between an electron and the phonons. There are two important laws, closely analogous to the laws of conservation of energy and momentum for two masses in collision. The quantity analogous to momentum for the phonon is a vector, called \vec{P}_γ , directed along the direction of propagation of the phonon, and having a magnitude given by the relationship between momentum and wavelength

$$P_\gamma = h(1/\lambda) = h/\lambda, \quad \vec{P}_\gamma \parallel \text{propagation direction} \quad (3.3)$$

In a transition in which an electron exchanges energy with the phonons, and changes its momentum from \vec{P}_1 to \vec{P}_2 , so that $\delta n_\gamma = \pm 1$ for one of the modes, one selection rule requires that

$$\vec{P}_2 - \vec{P}_1 + \delta n_\gamma \vec{P}_\gamma = 0. \quad (3.4)$$

This is analogous to conservation of momentum; actually it is based on far more subtle effects. The conservation of energy requires that

$$\varepsilon_2 + \delta n_\gamma h\nu_\gamma = \varepsilon_1 \quad (3.5)$$

where

$$\varepsilon_2 = P_2^2/2m, \quad \varepsilon_1 = P_1^2/2m \quad (3.6)$$

are the electron's energies before and after collision. The mass m need not be the mass of an electron but may instead be the "effective mass," a mass-like quantity of the same order as the electron mass which takes into account the influence of the periodic potential of the crystal structure upon the electron wave packet.

The effective mass concept represents a simplification that may not

necessarily be correct. In a cubic semiconductor, the electron waves can be "refracted" as are the longitudinal and transverse acoustical waves. The deviations from Ohm's law of Fig. 2 furnish evidence that the simplified assumption of equation (3.6) must in fact be replaced by the more general possibility. We shall return briefly to this point in Section 5.

In addition to the conservation of energy and momentum, there are two other approximate selection rules which, while not exact, are so nearly fulfilled that no appreciable error is introduced by using them:

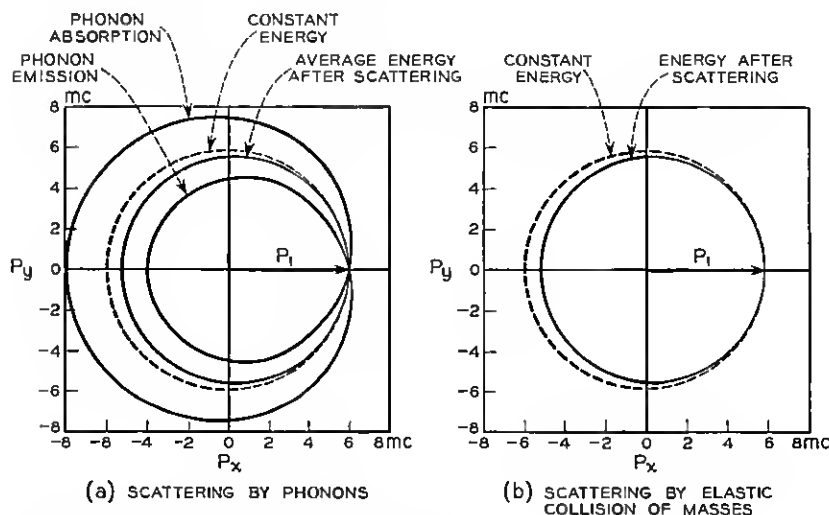


Fig. 4—Comparison of the scattering by acoustical phonons with the scattering of a small mass in elastic collision with a larger mass.

Only $\delta n_\gamma = \pm 1$ is allowed.

For the acoustical modes, only the longitudinal modes interact with electrons. (This restriction does not apply to optical phonons.)

Figure 4 shows the allowed transitions for an electron with initial momentum P_1 in the x -direction. If the energy of the phonons were zero, the allowed transitions would be to points on the sphere (or circle in Fig. 4) with $P_2 = P_1$. Since the energy of a phonon is

$$h\nu_\gamma = hc/\lambda = cP_\gamma = c|\vec{P}_2 - \vec{P}_1|, \quad (3.7)$$

however, the end points lie on the surfaces shown.

These surfaces do not differ much from the sphere, as may be seen by considering the final energy for an electron that reverses its motion by

phonon absorption. For this case

$$P_\gamma = P_2 + P_1 \quad (3.8)$$

and

$$(P_2^2 - P_1^2)/2m = cP_\gamma \quad (3.9)$$

so that the change in magnitude of momentum is

$$P_2 - P_1 = 2mc. \quad (3.10)$$

For an electron with energy kT and "thermal velocity"

$$v_T = (2kT/m)^{1/2}, \quad (3.11)$$

corresponding to 10^7 cm/sec at $300^\circ K$, the fractional change in momentum is

$$(P_2 - P_1)/P_1 = 2c/v_T = 2 \times 5.4 \times 10^5/10^7 = 0.11. \quad (3.12)$$

Thus the phonon absorption surface lies only 11% outside the constant energy sphere. Figure 4 is drawn for the case of $P_1 = 6mc$, or $v_1 = v_T$ for $32^\circ K$, for purposes of exaggerating the differences in the surfaces. (A further discussion of Fig. 4 is given in the appendices.)

For transitions with optical phonons, in the range of interest, $h\nu_\gamma$ is nearly independent of P_γ . Furthermore, the optical phonons have $h\nu_\gamma \doteq k 520^\circ K$ so that they are nearly unexcited at room temperature and have $n_\gamma = 0$ so that only $\delta n_\gamma = +1$ is allowed. For this case transitions can occur only if ϵ_1 is greater than $h\nu_{op}$ and the end surface is a sphere with

$$\epsilon_2 = \epsilon_1 - h\nu_{op}. \quad (3.13)$$

We shall neglect the role of the optical phonons until after a comparison between acoustical phonon processes and experiment has been made. We shall then show that they play an essential role in explaining Ryder's data.

3d. Energy Exchange and The Equivalent Sphere Problem

We shall here give in brief some results derived in the Appendices which permit us to show the equivalence of the problem of *acoustical phonon* scattering to a problem in gas discharges. This has two advantages: it enables us to take over the solution to the statistical problem from gas discharge theory, the second problem mentioned at the end of Section 3a, and to concentrate on the problem of the mechanism. In addition the equivalence makes it much easier to visualize the mechanism of energy losses.

According to the theory of phonon scattering, an electron is equally likely to be scattered from its initial direction of motion to any other. This implies that after an interaction the electron is equally likely to end in any unit

area of the surfaces of Fig. 4. The probability of being scattered per unit time is simply

$$1/\tau_1 = v_1/\ell \quad (3.14)$$

where v_1 is the speed and ℓ the mean free path; according to the theory ℓ is a function of the temperature T of the phonon system and is independent of v_1 . The time τ_1 is the mean free time or average time between collisions.

Figure 4 shows the average energy after collision. The Figure represents a case in which the average energy is somewhat smaller than the initial energy. This will be the case for a high energy electron, that is one with an energy greater than kT for the acoustical modes. The average loss in energy for a high energy electron is found to be

$$\langle \delta \mathcal{E} \rangle = -c^2 P_\gamma^2 / 2kT \quad (3.15)$$

where P_γ is the momentum change in the collision. This formula is analogous to the formula for energy loss if a light mass m strikes a heavy stationary mass M and transfers a momentum $\vec{P}_2 - \vec{P}_1 = \vec{P}_\gamma$ to it. The energy transfer is given by (3.15) if

$$M = kT/c^2 \quad (3.16)$$

since then the kinetic energy of the large mass is simply

$$P_\gamma^2 / 2M = c^2 P_\gamma^2 / 2kT. \quad (3.17)$$

The value of the mass which satisfies equation (3.16) for room temperature may be calculated from the previously quoted values of v_T and c :

$$M = kT/c^2 = mv_T^2/2c^2 = 170m, \quad (3.18)$$

a value which may certainly be considered large compared to m .

Equation (3.15) is not the complete expression for average energy change for a collision with momentum change P_γ and another term representing energy gain also occurs. If the complete expression is averaged over all final directions of motion, it is found that the average change of energy, which is obviously the average energy change per collision, is

$$\langle \delta \mathcal{E} \rangle = 4mc^2(1 - P_1^2/4mkT) = (4mkT/M) - (P_1^2/M). \quad (3.19)$$

This is the correct expression for the average gain in energy per collision of a light mass m colliding with a heavy mass M which is moving with the thermal energy appropriate to temperature T . This corresponds to a thermal velocity of

$$v_{TM} = (2kT/M)^{1/2} = 2^{1/2}c \quad (3.20)$$

for the large mass. The second term in (3.19) is just the average of (3.15) over all directions of motion after collision and represents the energy loss that would arise if M were initially stationary. The first term represents an energy transfer from M to m due to the thermal motion of the large mass.

Furthermore, if the light and heavy masses are perfectly elastic spheres, the scattering of m will be isotropic, just as is the case for the phonons. This shows that there is an almost perfect correspondence between the two mechanisms of scattering so that we are justified in using previously derived results for the sphere case and applying them to the phonon case.

To complete the equivalence we should introduce a density of large spheres so as to get the correct mean free path. There is nothing unique about this procedure, as there is about the mass M and temperature T , and we may make a large selection of choices for number of M -spheres per unit volume and radii of interaction so as to obtain the desired mean free path. Once any choice is made, of course, it will give the same mean free path independent of electron energy and may be held constant independent of the electric field.

3e. Acoustical Phonons and Electric Fields

We shall next give a very approximate treatment of mobility in low and high electric fields. The emphasis will be upon the interplay of the physical forces, the mathematical details being left to the Appendices or to references.

In the Ohm's law range, the field E is so small that the electrons have the temperature of the lattice. They have a velocity of motion of approximately

$$v_T = (2kT/m)^{1/2} \quad (3.21)$$

and a mean free time between collisions of

$$\tau = \ell/v_T. \quad (3.22)$$

The electric field accelerates the electron at a rate

$$a = qE/m \quad (3.23)$$

and imparts a velocity $a\tau$ in one mean free time. Since the collisions are spherical, the effect of the field is wiped out after each collision. The drift velocity is thus approximately

$$v_d = a\tau = (q\ell/mv_T)E. \quad (3.24)$$

An exact treatment which averages over the Maxwellian velocity distribution gives a value smaller by 25% and leads to

$$\mu_0 = 4q\ell/3\pi^{1/2}mv_T. \quad (3.25)$$

Since theory shows that ℓ varies as T^{-1} , the mobility should vary as $T^{-3/2}$. This prediction is in good agreement with experimental findings over the range of conditions for which the dominant scattering processes are those considered here.

Next we consider the effect of very large fields. Under these conditions an electron drifting in the direction of the field with drift velocity v_d acquires energy from the field at an average rate

$$(d\mathcal{E}/dt)_{\text{due to } E} = v_d q E. \quad (3.26)$$

If this power is large enough, the electrons will be unable to dissipate energy sufficiently rapidly to the phonons that they can maintain their normal temperature. As a result their average energy mounts, after the field is initially applied, until they can furnish energy to the phonons fast enough to maintain a steady state. Under these conditions the sum of the two rates is zero

$$(d\mathcal{E}/dt)_{\text{due to } E} + (d\mathcal{E}/dt)_{\text{due to phonons}} = 0. \quad (3.27)$$

If the field is high enough, there may be no steady state solution. This can occur if the ability of the phonons to remove energy decreases with increasing energy. Such cases play an essential role in the theory of dielectric breakdown.⁸ In them it is concluded that electrons will gain sufficient energy from the field so that they can produce secondary electrons which repeat the process thus producing avalanches. For the cases with which we are concerned, theory indicates that the energy losses increase rapidly with the energy of the electron while the power input decreases because of decreasing mobility so that a steady state will thus occur.

In order to estimate the drift velocity for the steady state we must introduce expressions for the two powers involved. For this purpose we assume that an electron has on the average a speed v_1 and we calculate the power to phonons as the average energy loss per collision for this velocity times the rate of collision, v_1/ℓ . For $v_1 \gg v_T$, we can neglect the effect of motion of the M spheres and thus obtain from (3.19)

$$(d\mathcal{E}/dt)_{\text{phonons}} = -(v_1/\ell) m^2 v_1^2 / M. \quad (3.28)$$

The mobility will be less because of the higher collision rate so that the drift velocity in the field will be approximately

$$v_d = (q\ell/mv_1)E. \quad (3.29)$$

The power furnished by E will be

$$(d\mathcal{E}/dt)_{\text{due to } E} = (q^2\ell/mv_1)E^2. \quad (3.30)$$

⁸ See the references to Fröhlich and Seitz in Section 1.

The steady state condition then leads to

$$v_1 = (q\ell E/m)^{1/2} (M/m)^{1/4} \quad (3.31)$$

and to

$$\begin{aligned} v_d &= (q\ell E/m)^{1/2} (m/M)^{1/4} \\ &= (\sqrt{2}cq\ell E/mv_T)^{1/2} \cong (c\mu_0 E)^{1/2}. \end{aligned} \quad (3.32)$$

The treatment⁹ based on accurate statistics for the equivalent sphere model leads to

$$v_d = 1.23(c\mu_0 E)^{1/2}. \quad (3.33)$$

The transition between the high field behavior and low field behavior should occur in the neighborhood of a critical field E_c at which both limiting forms give the same v_d :

$$v_d = \mu_0 E_c = 1.23(c\mu_0 E_c)^{1/2}, \quad (3.34)$$

leading to

$$E_c = 1.51 c/\mu_0 \quad (3.35)$$

and to a drift velocity, which shall be referred to as the *critical velocity*, of

$$v_{dc} = 1.51c \quad (3.36)$$

if Ohm's law held to a field as high as E_c . The drift velocity can be expressed in terms of E_c by the equation

$$v_d = \mu_0 (EE_c)^{1/2} \quad (3.37)$$

for values of E much greater than E_c .

It is interesting to note that this initial field is just that which would give electrons a drift velocity corresponding to the thermal motion of M -masses. This seems a natural critical field. For it the effect of random motion of M would be suppressed by the systematic drift velocity so that the transfer of thermal energy to the electrons would be much reduced. This value of E_c corresponds to much smaller initial fields than are sometimes proposed. For example, one frequently encounters proposals that Ohm's law should hold up to the condition that $v_d = v_T$. This would correspond to 10 times higher field at 300°K than that obtained. Another criterion is that the energy gained in one mean free path, $q\ell E$, should be equal to kT . This is substantially equivalent and corresponds to $v_d = v_T/2$.

⁹ *Druyvesteyn Physica* 10, 61, 1930. This paper is reviewed by S. Chapman and T. G. Cowling in "The Mathematical Theory of Non-Uniform Gases," Cambridge at the University Press, 1939, page 347. (The factor is $0.897 (18\pi/8)^{1/4} = 1.23$.)

For comparison with experiment we note that for a value of

$$E = 4E_c = 6.04c/\mu_0 \quad (3.37)$$

such that if Ohm's law held

$$v_d = 6.04c, \quad (3.38)$$

the value of v_d should be less than half the value predicted by Ohm's law. We shall shortly discuss the discrepancy between this prediction and experiment.

The "temperature" of the electrons may be conveniently expressed in terms of the ratio E/E_c . Since the electrons for the high field case are not in a Maxwellian distribution of velocities, one cannot define their "temperature" unambiguously. As a measure of their temperature we shall take their average kinetic energy divided by k . This leads to a ratio of electron temperature $T(E)$ to crystal temperature T of $2v_1^2/3v_T^2$. Since to a first approximation the ratio of mobilities at low and high fields is $4v_1/3\pi^{1/2}v_T$, the ratio of temperatures is

$$\frac{T(E)}{T} = \frac{3\pi}{8} \left[\frac{\mu_0}{v_d(E)/E} \right]^2 = \frac{3\pi E}{8E_c}. \quad (3.40)$$

This ratio may also be thought of in terms of the square of the ratio of drift velocity on the extrapolated Ohm's law line to the drift velocity on the $E^{1/2}$ line:

$$T(E)/T = (3\pi/8)[\mu_0 E/v_d(E)]^2. \quad (3.41)$$

Either of these equations may be used to estimate electron temperature from the data in the range in which the $E^{1/2}$ formula is a good approximation.

4. COMPARISON BETWEEN THEORY AND EXPERIMENT

4a. Discrepancy in Critical Field

In Fig. 5 we repeat Ryder's data of Fig. 2 together with data on an additional sample at 77°K. This new sample is considered more reliable than the first since its low field resistivity varies in just the proper ratio [see (3.25) and subsequent text] of $(298/77)^{3/2}$ compared to its value at room temperature. Also we show the theoretical curves that will be discussed below.

The deviations of the data from Ohm's law do not occur at fields as low as those predicted in Section 3e. For $c = 5.4 \times 10^5$ cm/sec., the critical drift velocity should be

$$v_{dc} = 1.51c = 8.2 \times 10^5 \text{ cm/sec.} \quad (4.1)$$

It is seen that Ohm's law is followed to several times higher velocities with negligible deviations. The deviations should be a factor of 2 at the field corresponding to

$$v_d = 6.04c = 3.26 \times 10^8 \text{ cm/sec.} \quad (4.2)$$

on the Ohm's law line. The deviations are actually much less.

Another important difference between the data and the theory of Section 3 is that the experimental points do not continue on a straight line with slope 1/2 but instead tend to flatten out with a roughly constant drift velocity.

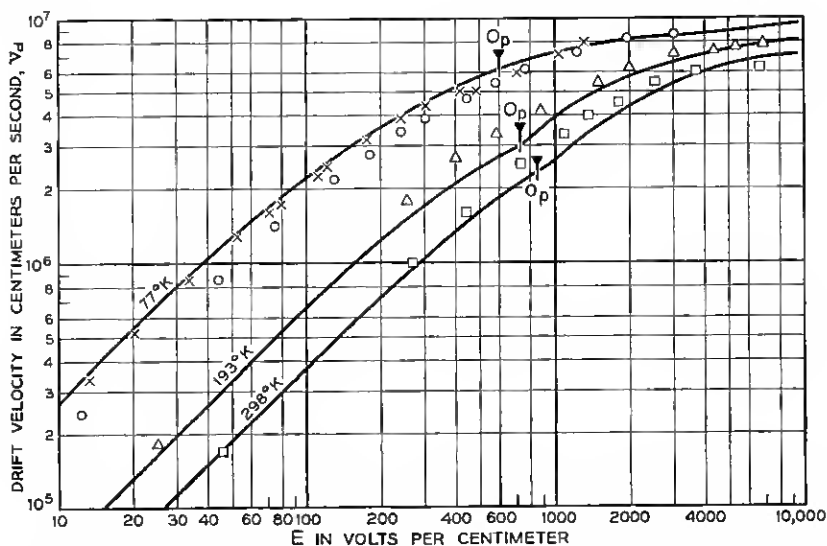


Fig. 5—Comparison of E. J. Ryder's experimental data and the statistical theory of Appendix A7.

Three theoretical curves are shown. These are based on an approximate treatment that includes the effect of the optical transitions. Due to the approximation, the optical modes are neglected below the points marked Op on the Figure. This approximation also leads to a discontinuity in slope at these points; in a more accurate treatment, this bump would be smoothed out. The optical modes play the least role for the curve at 77°K and for this theory fits experiment within experimental accuracy if a value of

$$v_{dc} = 2.6 \times 10^6 \text{ cm/sec.} \quad (4.3)$$

is used. This value is 3.2 times larger than the value given by equation (3.36) using $c = 5.4 \times 10^5$ cm/sec, the value appropriate for longitudinal phonons.¹⁰ The interpretation of this discrepancy, which we refer to as the "low field" discrepancy, is discussed in Section 5. It does not, of course, imply an error in the value of the sound velocity, but instead an error in the theory leading to the formula for critical velocity in terms of sound velocity.

Although an exact theory along the lines discussed in Section 5 has not been developed, it appears evident that its chief effect will be to increase energy interchange with the phonons by a factor of 3.2 squared or approximately 10. This increase can be effected in a mathematically equivalent way by introducing an *effective velocity* for dealing with phonon energies which is 3.2 times larger than the true velocity of longitudinal waves. The approximate theory in the Appendices uses this procedure.

We may remark in passing that only two constants were arbitrarily chosen to fit the curves to the data. One of these was the effective velocity $c = 1.73 \times 10^6$ cm/sec. which is 3.2 times larger than the speed of longitudinal waves. The other was the mobility of electrons at room temperature. Three other constants were chosen from independent estimates of the properties of the crystal. One of these is $h\nu$ for the optical modes for which a value of $k520^\circ\text{K}$ was used; another is the effective electron mass, for which the free electron mass was used; and a third was the interaction constant for optical modes, which was set equal to that for the acoustical modes. The meaning of these terms is discussed in the Appendices.

4b. *The Effect of the Optical Modes*

We shall next discuss briefly the role of the optical modes before remarking on a theory of the low field discrepancy.

As discussed above the optical modes can act only if $\mathcal{E}_1 > h\nu_{op}$. Theory indicates, however, that when they do come into action they are much more effective than the acoustical modes. On the basis of these ideas, we can see how they can act to give a limiting drift velocity that does not increase with increasing electric field. For purposes of this illustration we shall imagine that so high an electric field is applied that an electron may be accelerated from $P_1 = 0$ to $P_2 = (2mh\nu_{op})^{1/2}$, at which its energy equals $h\nu_{op}$, in so short a time that it is not scattered by acoustical modes. As soon as it reaches P_2 , we assume that it is scattered by the optical modes, loses all its energy and returns to zero energy. This process then repeats, the period being

¹⁰ This is the velocity of longitudinal waves in the [110] direction as reported by W. L. Bond, W. P. Mason, H. J. McSkimin, K. M. Olsen and G. K. Teal, *Phys. Rev.* **73**, 549 (1948). See "Electrons and Holes in Semiconductors," page 528, for the reason for using this wave.

P_2/qE since $dP_2/dt = qE$. The average momentum is evidently $P_2/2$ and the average velocity is

$$v_d = P_2/2m = (h\nu_{0y}/2m)^{1/2} \quad (4.4)$$

and is independent of E . The optical modes correspond to a temperature of about 520°K and this leads to

$$v_d = 6.3 \times 10^6 \text{ cm/sec.} \quad (4.5)$$

in general agreement with the observed value.

The theory in the appendices indicates that both optical and acoustical modes are active simultaneously and their interplay leads to the theoretical curves shown. (In the Appendices a further discussion is presented and some additional data are compared with theory.)

The tendency of the theoretical curves to fall below the data for 193°K and 298°K for field values below the optical point is thought to arise largely from the approximations employed in the theory. The approximations neglect the ability of the optical modes to enable the electrons to lose energy for fields below the indicated value. Actually some electrons will be scattered by the optical modes and this will contribute in an important way to holding the temperature down and the mobility up. A correct treatment would, therefore, raise the theoretical curve appreciably in the region where it deviates most from the data.

4c. Electron "Temperatures"

From the theory it follows that the average electron energies correspond to about 520°K at the points marked Op on Fig. 5. The highest point on the 298°K curve corresponds to $\sim 700^\circ\text{K}$ and the highest point on the 77°K curve corresponds to 550°K. For this last case the electron temperature is more than seven times as high as that of the atomic vibrations. In the appendix we quote some other earlier data of Ryder's that indicates electron temperatures of about 4000°K while the crystal itself remains at room temperature.

5. AN EXPLANATION OF THE LOW FIELD DISCREPANCY

The failure to deviate from Ohm's law at the low fields predicted indicates that the electrons can dissipate their excess energy more effectively than would be expected on the basis of their mobility. This conclusion is forced on us by the observation that they apparently retain their thermal distribution and normal mobility to higher fields than predicted. It is not possible to explain the discrepancy by assuming a large or a small value for the effective mass, since the value of the effective mass does not enter into the final comparison with experiment.

It is possible, however, to explain the discrepancy by assuming that the effective mass is not single valued. This assumption corresponds to the case in which the surface in the Brillouin zone belonging to a single energy is not a sphere but instead a complex surface of two or three sheets. Such surfaces have been found as a result of numerical calculations for certain crystals¹¹ and it has also been shown that such surfaces are to be expected in general¹² if the energy at the bottom of the conduction band is degenerate. It appears necessary to assume that such complex surfaces occur in order to explain magnetoresistance effects.¹³

In terms of Fig. 4, this theory replaces the circular energy contours by deeply re-entrant curves. Transitions from peak to peak of the curves result in large energy transfers to the phonons and hence more effective energy losses. This effect can occur without a compensating change in the effective mass involved in the mobility and, as a result, the critical field may be increased by a large factor. A preliminary analysis indicates that in order to increase the critical field by a factor of 3 a value of about 3 is also required for the ratio of maximum to minimum momentum for the energy surface. A similar analysis of magnetoresistance leads to a factor about 50% larger in order to account for the increases in transverse resistance of about 7-fold observed by Suhl.¹⁴ At the time of writing, therefore, the author feels that both the critical field data at low fields and the magnetoresistance data require a modification of the effective mass picture and that the same modification may well explain both sets of data.

I am indebted to E. J. Ryder, whose experimental results provoked the analysis presented in this paper, to F. Seitz and J. Bardeen for several helpful discussions, to Gregory Wannier for an introduction to the analogous case in gas discharge theory and to Esther Conwell for help with the manuscript.

I shall also take this opportunity to express my appreciation to C. J. Davisson. The opportunity to work in his group was a large factor in my decision to come to Bell Telephone Laboratories, where I enjoyed his stimulating companionship while assigned to his group, and later as well.

APPENDICES

A.1 INTRODUCTION AND NOTATION

The problem of energy exchange between the electrons and the phonons requires a somewhat more sophisticated treatment than does the problem of mobility at low fields. In order to present the theory of energy exchange,

¹¹ W. Shockley, *Phys. Rev.* 50, 754 (1936).

¹² W. Shockley, *Phys. Rev.* 78, 173 (1950).

¹³ W. Shockley, *Phys. Rev.* 79, 191 (1950).

¹⁴ H. Suhl, *Phys. Rev.* 78, 646 (1950). Suhl finds increases in resistance in transverse fields as high as 7-fold.

it is necessary to reproduce a large amount of the material dealt with in ordinary conductivity theory. We do this in a somewhat abbreviated form expanding the exposition on the points particularly pertinent to the theory of energy losses.

For convenience we reproduce here a number of the more important symbols. The references indicated refer to places where they are discussed in the text.

- a = lattice constant; Fig. 3.
- c = speed of longitudinal acoustical wave; Equ. (3.2).
- c_{11} = average longitudinal elastic constant; Equ. (A4.1).
- e = base of Naperian logarithms.
- E = electric field.
- \mathcal{E} = energy.
- \mathcal{E}_{1n} and \mathcal{E}_{2n} ; Equ. (A4.1) and (A7.9).
- $h = 2\pi \hbar$ = Planck's constant.
- k = Boltzmann's constant.
- ℓ = mean free path for electron due to scattering by acoustic phonons; (A4.3).
- ℓ_{op} = describes scattering by optical phonons; (A7.19).
- m = effective mass of electron.
- M = mass in equivalent mass treatment; (A5.8).
- \vec{P} = "crystal momentum" of electron = \hbar times its wave number.
- V = volume of crystal.
- Δ = dilation; (A4.1) and (A7.10).
- ν = frequency of normal mode.
- ν_{op} = frequency of optical mode (used in Section 4 only); Equ. (4.5).

A.2 THE PROBABILITY OF TRANSITION INTO ENERGY RANGE $\delta\mathcal{E}_2$

In this section we consider an electron initially with energy \mathcal{E}_1 and momentum \vec{P}_1 , which for convenience we take to be along the P_z -axis, and we evaluate the probability that it make a transition to states with energies in the range \mathcal{E}_2 to $\mathcal{E}_2 + \delta\mathcal{E}_2$. We shall assume that the crystal is elastically isotropic so that for the spherical energy surface approximation employed, i.e. equation 3.6, the scattering will be symmetrical about the P_z -axis. The end states, \vec{P}_2 , may, therefore, be considered in groups lying in the range $d\mathcal{E}_2, d\theta$ where θ is the angle between \vec{P}_1 and \vec{P}_2 . These states lie in a ring in \vec{P} -space whose volume is

$$2\pi P_2 \sin \theta P_2 d\theta dP_2 = 2\pi m P_2 \sin \theta d\theta d\mathcal{E}_2 \quad (\text{A2.1})$$

The number of end states in $d\theta d\mathcal{E}_2$ space is thus¹⁵

$$(V/h^3) 2\pi m P_2 \sin \theta d\theta d\mathcal{E}_2 \equiv \rho d\theta d\mathcal{E}_2 \quad (\text{A2.2})$$

(The density ρ introduced above is used below in calculating the transition probability; since spin is conserved in the transitions of interest, the density of possible end states in phase space is $1/h^3$ instead of $2/h^3$.)

The transitions will occur between states of the entire system, electron plus phonons, which conserve energy. The transition of the electron from \vec{P}_1 to \vec{P}_2 requires a compensating change in the phonon field.¹⁶ The conservation laws allow two possibilities: (I) *phonon emission*; the longitudinal acoustical mode with

$$P_\alpha \equiv \hbar \vec{k}_\alpha = -(\vec{P}_2 - \vec{P}_1) \quad (\text{A2.3})$$

undergoes a change

$$n_\alpha \rightarrow n_\alpha + 1 \quad (\text{A2.4})$$

with a change in energy for the electron of

$$\mathcal{E}_2 - \mathcal{E}_1 = -\hbar \omega_\alpha = -\hbar c/\lambda = -cP_\alpha \quad (\text{A2.5})$$

where c is the velocity of the longitudinal phonons that are chiefly responsible for the scattering. These relationships lead to conservation of the sum of \vec{P} for the electron plus $\sum n_\alpha \vec{P}_\alpha$ for the phonons. The other possibility is (II) *phonon absorption*, for this case

$$\vec{P}_\beta \equiv \hbar \vec{k}_\beta = (\vec{P}_2 - \vec{P}_1) \quad (\text{A2.6})$$

$$n_\beta \rightarrow n_\beta - 1 \quad (\text{A2.7})$$

$$\mathcal{E}_2 - \mathcal{E}_1 = +cP_\beta \quad (\text{A2.8})$$

again with conservation of the sum of P vectors.

If we denote by \mathcal{E} the energy of the electron after collision plus the change in phonon energy, then the requirement of equality for energy before and after collision gives

$$\mathcal{E} = \mathcal{E}_2 + \delta n_\gamma c P_\gamma = \mathcal{E}_1 \quad (\text{A2.9})$$

where $\delta n_\gamma = +1$ is the phonon emission or α surface and $\delta n_\gamma = -1$ is the phonon absorption or β surface of Fig. 4.

¹⁵ The notation in this appendix follows closely that of W. Shockley, "Electrons and Holes in Semiconductors," D. van Nostrand (1950) to which we shall refer as *E and II in S*. See page 253 for a similar treatment of ρ .

¹⁶ This condition is analogous to one for the conservation of momentum but has a different interpretation. See for example *E and II in S*, p. 519 equation (15).

We shall next insert these symbols into the conventional expression for transition probability. We consider a system described by one or more sets of quantum numbers, say x_1, x_2, \dots, x_n which may take on discrete but closely spaced values so that the numbers of states lying in a range dx_1, \dots, dx_n is

$$\rho(x_1, \dots, x_n) dx_1 \cdots dx_n. \quad (\text{A2.10})$$

The system may make a transition from an initial state φ_0 and energy ε_0 to another state φ_i of the same energy between which there is a matrix element U_{0i} . The total probability of the system making a transition per unit time to the range of quantum numbers dx_2, dx_3, \dots, dx_n is then¹⁷

$$W_{0i} dx_2 \cdots dx_n = (2\pi/\hbar) |U_{0i}|^2 [\rho/(\partial\varepsilon_i/\partial x_1)] dx_2, \dots, dx_n \quad (\text{A2.11})$$

where $\partial\varepsilon_i/\partial x_1$ is evaluated where $\varepsilon_i = \varepsilon_0$; if for the range dx_2, \dots, dx_n of the other quantum numbers there is no x_1 value that gives $\varepsilon_i = \varepsilon_0$, then the transition does not occur.

We shall apply this to our case letting $\theta = x_1$ and $\varepsilon_2 = x_2$. The expression $\partial\varepsilon_i/\partial x_1$ then becomes

$$\frac{\partial\varepsilon_i}{\partial x_1} \equiv \left(\frac{\partial\varepsilon}{\partial\theta}\right)_{\varepsilon_2} = \delta n_\gamma c \left(\frac{\partial P_\gamma}{\partial\theta}\right)_{\varepsilon_2} \quad (\text{A2.12})$$

where

$$\begin{aligned} \frac{\partial}{\partial\theta} P_\gamma &= \frac{\partial}{\partial\theta} |\vec{P}_2 - P_1| = \frac{\partial}{\partial\theta} (P_2^2 + P_1^2 - 2P_1P_2 \cos\theta)^{1/2} \\ &= P_1P_2 \sin\theta/P_\gamma. \end{aligned} \quad (\text{A2.13})$$

We then obtain, for $W_{12} d\varepsilon_2$, the probability per unit time of transition of the electron from \vec{P}_1 to states with energies between ε_2 and $\varepsilon_2 + d\varepsilon_2$, the expression

$$\begin{aligned} W_{12} d\varepsilon_2 &= (2\pi/\hbar) |U|^2 (V/\hbar^3) 2\pi m P_2 \sin\theta \times (P_\gamma/c \delta n_\gamma P_1 P_2 \sin\theta) d\varepsilon_2 \\ &= (V/2\pi\hbar^4) m |U|^2 (P_\gamma/c \delta n_\gamma P_1) d\varepsilon_2 \\ &= (V/2\pi\hbar^4) m |U|^2 (P_\gamma/P_1) (-dP_\gamma); \end{aligned} \quad (\text{A2.14})$$

where the negative coefficient of dP_γ is without significance except for its relationship to the selection of the limits of integration. In subsequent equations we shall disregard the sign convention which relates $d\varepsilon_2$ to dP_γ ; no

¹⁷ See L. I. Schiff "Quantum Mechanics," McGraw-Hill Book Co. (1949), equation (29.12). The additional factor $1/(\partial\varepsilon_i/\partial x_1)$ converts the ρ used here to that of Schiff, which latter is number of states per unit energy range.

error is introduced provided the subsequent integrations are always in the direction of increasing values for the variables concerned.

A.3 THE ALLOWED RANGES FOR P_γ

An electron with an energy corresponding to room temperature can change its energy by only a small fraction in a one phonon transition. The extremes occur for $\theta = \pi$ corresponding to complete reversal of direction. For this case we have

$$\begin{aligned}\varepsilon_2 - \varepsilon_1 &= (P_2^2 - P_1^2)/2m = -\delta n_\gamma c P_\gamma \\ &= -\delta n_\gamma c (P_2 + P_1)\end{aligned}\quad (\text{A3.1})$$

so that

$$P_2 - P_1 = -\delta n_\gamma 2mc \equiv -2\delta n_\gamma P_0. \quad (\text{A3.2})$$

Thus the limiting values of P_2 differ from P_1 by

$$\pm 2P_0 = \pm 2mc \quad (\text{A3.3})$$

in keeping with the results shown in Fig. 4. [For $v_1 = P_1/m = 10^7$ cm/sec, corresponding to $\varepsilon_1 = 0.025$ electron volts, and $c = 5.4 \times 10^5$ cm/sec, it is seen that P_2 and P_1 differ by 10%.] For this case the range of P_γ is

$$\text{phonon emission, } \delta n_\alpha = +1, P_\alpha \text{ from } 0 \text{ to } 2(P_1 - P_0) \quad (\text{A3.4})$$

$$\text{phonon absorption, } \delta n_\beta = -1, P_\beta \text{ from } 0 \text{ to } 2(P_1 + P_0). \quad (\text{A3.5})$$

A singularity occurs for $P_1 = P_0$. For this case phonon emission becomes impossible and the inner curve of Fig. 4 shrinks to zero; in Fig. A1 we show the sequence of shrinkage. The value of ε_1 for this condition corresponds to thermal energy for a temperature of less than 1°K. Under the conditions for which we shall compare theory and experiment, a negligible number of electrons lie in this range. Accordingly we shall use the above limits in calculations and neglect the small errors introduced.

A.4 THE MATRIX ELEMENT AND THE MEAN FREE PATH

The matrix element may be written in the form¹⁸

$$|U|^2 = \varepsilon_{1n}^2 (2n_\gamma + 1 + \delta n_\gamma) P_\gamma c / 4V c_{ll} \quad (\text{A4.1})$$

where ε_{1n} is the derivative of the edge of the conduction band in respect to dilatation of the crystal and c_{ll} is the elastic constant for longitudinal

¹⁸ See *E and H in S*, page 528, equation 31. The second expression in equation 31 of this reference is in error by omission of a factor $\hbar\omega_{ka} = cP_\gamma$.

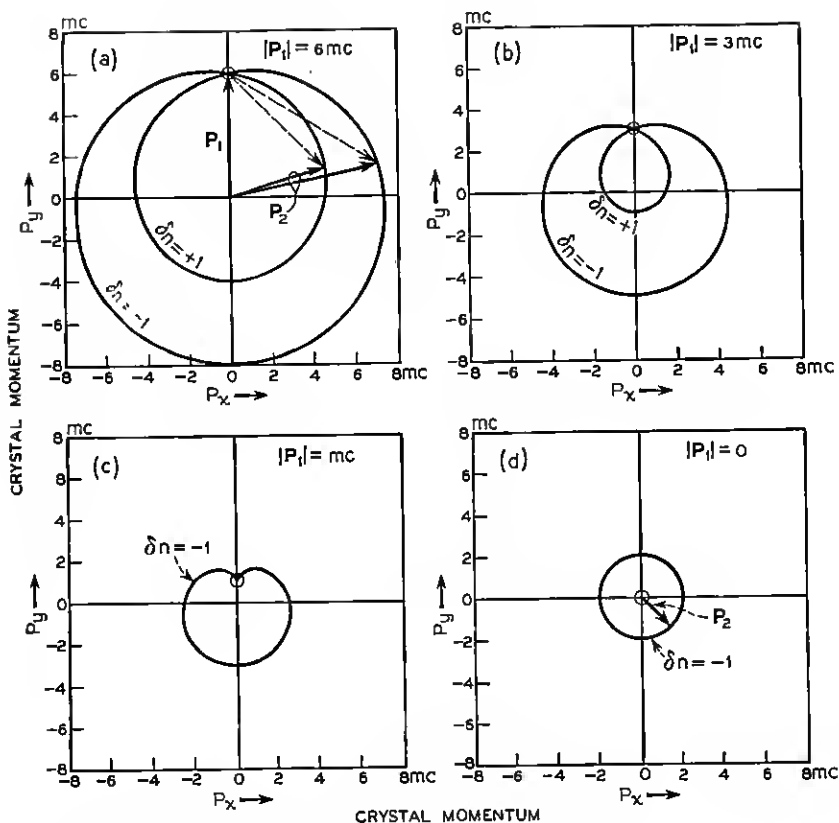


Fig. A1—Initial and Final Values of \vec{P} for Transitions which conserve energy.

(a) The two nearly spherical surfaces for $|\vec{P}_1| = 6 mc$.

(b) The two surfaces for $|\vec{P}_1| = 3 mc$.

(c) For an electron with $|\vec{P}_1| = mc$, energy loss is impossible.

(d) The case of $|\vec{P}_1| = 0$.

waves. Inserting this in the expression (A2.14) for $W_{12} d\epsilon_2$, we obtain

$$\begin{aligned}
 W_{12} d\epsilon_2 &= (V/2\pi\hbar^4) m [\epsilon_{1n}^2 P_\gamma c / 4V c \ell] \\
 &\quad \times (2n_\gamma + 1 + \delta n_\gamma) (P_\gamma / P_1) dP_\gamma \quad (\text{A4.2}) \\
 &= (1/\ell) (1/8mP_1) (2n_\gamma + 1 + \delta n_\gamma) (cP_\gamma / kT) P_\gamma dP_\gamma
 \end{aligned}$$

where we have used the symbol ℓ to represent

$$\ell = \pi \hbar^4 c \ell / m^2 \epsilon_{1n}^2 kT \quad (\text{A4.3})$$

because, as we shall shortly show, ℓ is the mean free path for electrons.

For the cases with which we shall be concerned, the values of n_γ may be approximated by classical equipartition. This may be seen from the fact that largest energy phonons correspond approximately to an energy of

$$\begin{aligned} cP_\gamma &\doteq 2cP_1 = (4cm/P_1)P_1^2/2m \\ &\doteq (4c/v_1)kT. \end{aligned} \quad (\text{A4.4})$$

Their energies will, therefore, be considerably less than kT . For large increases in electron energy in high fields, however, this approximation may not be adequate. At room temperature $cP_\gamma/kT \doteq 0.2$ and the critical range will correspond approximately to an increase of about 10 fold of electron temperature above the temperature of the crystal. Under these conditions cP_γ deduced from equation (A4.4) will be about $2kT$ for the most energetic phonons; for this condition, however, \vec{P}_γ lies at the edge of the Brillouin zone and dispersive effects must be considered. In this treatment we shall not investigate further these limits and shall in general assume that $cP_\gamma < kT$.

We shall next derive an expression for the mean free path and verify that the scattering is isotropic. These results can be derived more simply and directly from the matrix element by neglecting (P_0/P_1) and (cP_α/kT) from the outset. For the treatment of energy losses that follows, we cannot make these approximations. We shall, however, make them in the remainder of this section thus establishing that our more general formulation reduces correctly to the more convenient and simpler formulation usually used.

For the condition under which equilibrium applies we may approximate n_γ as follows:

$$n_\gamma = 1/[(\exp cP_\gamma/kT) - 1] \doteq (kT/cP_\gamma) - \frac{1}{2}. \quad (\text{A4.5})$$

Then, for the phonon emission or α case, the contribution to $W_{12} d\mathcal{E}_2$ becomes

$$W_{12} d\mathcal{E}_2 = (4m\ell P_1)^{-1}[1 + (cP_\alpha/2kT)]P_\alpha dP_\alpha \quad (\text{A4.6a})$$

and for the phonon absorption case, it becomes

$$W_{12} d\mathcal{E}_2 = (4m\ell P_1)^{-1}[1 - (cP_\beta/2kT)]P_\beta dP_\beta. \quad (\text{A4.6b})$$

We shall use these expressions later for the calculation of energy exchange, in which case the terms in $cP_\alpha/2kT$, which favor phonon emission, play an important role. In order to check the expression for mean free path we neglect these terms, however, and also approximate the integral of $P_\alpha dP_\alpha$ by $2P_1^2$ rather than $2(P_1 - P_0)^2$. The total probability of transition from state

\vec{P}_1 , which should be taken to be $1/\tau_1$ where τ_1 is the mean free time, is then

$$1/\tau_1 = W_1 = (4m\ell P_1)^{-1} 4P_1^2 = (P_1/m)/\ell = v_1/\ell. \quad (\text{A4.7})$$

This is just the relationship appropriate to the interpretation of ℓ as a mean free path between collisions.¹⁹ It does not follow that τ_1 is the relaxation time for the current, however, unless the average velocity after collision is zero. We shall next show that the average velocity after collision is zero to the same degree of approximation used above by showing that scattering into any solid angle of directions is simply proportional to the solid angle, i.e. the direction of motion after collision is random.

The conclusion that the scattering is nearly isotropic follows from the approximate proportionality of probability to $P_\gamma dP_\gamma$. Since P_2 is nearly equal to P_1 and substantially independent of θ , we may write

$$\begin{aligned} P_\alpha dP_\alpha &= \frac{1}{2} d(P_\alpha)^2 = \frac{1}{2} d(2P_1^2 - 2P_1^2 \cos \theta) \\ &= -P_1^2 d \cos \theta = P_1^2 \sin \theta d\theta. \end{aligned} \quad (\text{A4.8})$$

The last term is simply proportional to the solid angle lying in range $d\theta$; hence the end states are distributed with uniform probability over all directions and the scattering is isotropic.

A5. APPROXIMATE EQUIVALENCE TO ELASTIC SPHERE MODEL

In this section we shall show that on the average the energy exchange between the electron and the phonons when the electron is scattered through an angle θ is very similar in form to that corresponding to elastic collisions between spheres with the phonons represented by a mass much greater than the electrons. If dP_α and dP_β correspond to scattering through angles between θ and $\theta + d\theta$, then the energy loss for phonon emission is cP_α and the energy gain for absorption is cP_β . The relative probabilities of loss and gain are given by equations (A4.6) and from these it is found that the average energy gain is

$$\begin{aligned} \langle \delta \mathcal{E} \rangle &= \frac{cP_\beta[1 - (cP_\beta/2kT)]P_\beta dP_\beta - cP_\alpha[1 + (cP_\alpha/2kT)]P_\alpha dP_\alpha}{[1 - (cP_\beta/2kT)]P_\beta dP_\beta + [1 + (cP_\alpha/2kT)]P_\alpha dP_\alpha} \\ &= \frac{c[P_\beta^2 dP_\beta - P_\alpha^2 dP_\alpha] - (c^2/2kT)(P_\beta^3 dP_\beta + P_\alpha^3 dP_\alpha)}{[1 - (cP_\beta/2kT)]P_\beta dP_\beta + [1 + (cP_\alpha/2kT)]P_\alpha dP_\alpha}. \end{aligned} \quad (\text{A5.1})$$

Since we are concerned chiefly with cases in which $P_0 \ll P_1$, $P_2 \doteq P_1$, and $cP_\beta/kT \ll 1$, we may set

$$P_\alpha \doteq P_\beta \doteq P_\gamma \equiv 2P_1 \sin(\theta/2) \quad (\text{A5.2})$$

¹⁹ See *E and H in S*, Chapter 11.

where P_γ corresponds to neglecting the energy change of the electron on collision. This approximation is not good enough for the first term in (A5.1) which involves $P_\beta - P_\alpha$. In order to evaluate this first term we note that the relationships

$$P_\alpha = P_\gamma[1 - (P_0 P_\gamma / 2P_1^2)] \quad (\text{A5.3a})$$

$$P_\beta = P_\gamma[1 + (P_0 P_\gamma / 2P_1^2)] \quad (\text{A5.3b})$$

may be derived up to the first order in P_0 . This permits us to write

$$\begin{aligned} P_\beta^2 dP_\beta - P_\alpha^2 dP_\alpha &\doteq (\tfrac{1}{3}) d[(P_\beta - P_\alpha)(3P_\gamma^2)] \\ &= d[P_0 P_\gamma^4 / P_1^2] = 4(P_0 P_\gamma^2 / P_1^2) P_\gamma dP_\gamma. \end{aligned} \quad (\text{A5.4})$$

Hence

$$\langle \delta \mathcal{E} \rangle = 2(c P_0 P_\gamma^2 / P_1^2) - c^2 P_\gamma^2 / 2kT. \quad (\text{A5.5})$$

The second term is proportional to the (average change in momentum)² for collision by angle θ . It thus corresponds to energy which would be transferred to an initially stationary mass $M \gg m$ by the colliding electron provided we take

$$M = kT/c^2. \quad (\text{A5.6})$$

That this mass is much greater than the electron's mass may be seen in terms of v , the velocity of a thermal electron:

$$mv_1^2/2 = kT. \quad (\text{A5.7})$$

From this we obtain

$$M = m(v_1/c)^2/2 \doteq 170m \quad (\text{A5.8})$$

at room temperature where $v_1 \doteq 10^7$ cm/sec while $c \doteq 5.4 \times 10^5$ cm/sec.

The first term may then be interpreted as follows:

$$2c P_0 P_\gamma^2 / P_1^2 = 2c^2 m P_\gamma^2 / P_1^2 = 2(kTm/M)(P_\gamma^2 / P_1^2) \quad (\text{A5.9})$$

If this is averaged over all angles θ , the P_γ^2 / P_1^2 term becomes 2; the energy gain is then just that picked up by a mass m colliding with a mass M moving with a Maxwellian distribution at temperature T as may be seen as follows: For this case the velocity v_M of M parallel to the line of centers on collision imparts an added velocity $2v_M$ to the electron and, on the average, an energy

$$(\tfrac{1}{2})m \langle (2v_M)^2 \rangle = 2m \langle v_M^2 \rangle = 2m kT/M \quad (\text{A5.11})$$

since $M\langle v_M^2 \rangle / 2 = kT/2$. In addition, however, there is an effect due to relative velocity: when v_M is directed so as to increase the closing velocity, the probability of collision is increased. Due to this effect, collisions with higher relative velocity are favored and as a result the energy transferred due to the v_M effect is just doubled³⁰ leading to a total contribution of

$$(\text{energy transfer due to } v_M) = 4mkT/M. \quad (\text{A5.10})$$

This is just to the first term of (A5.5) when averaged over all values of θ .

Thus the average of the gain in energy term in (A5.5) is just that corresponding to interactions with heavy masses M in thermal agitation. The difference is that in the sphere model the average energy gain term is independent of θ , whereas in the phonon case it varies as P_γ^2/P_1^2 and approaches zero for forward scattering so that the dependence upon angle is different. The energy loss term, however, is correctly represented by the sphere model.

The average value of $\langle \delta \mathcal{E} \rangle$ averaged over all values of θ is denoted by $\langle \delta \mathcal{E} \rangle_{P_1}$. Since P_γ^2 averaged over θ is $2P_1^2$, we obtain

$$\begin{aligned} \langle \delta \mathcal{E} \rangle_{P_1} &= 4cP_0 - c^2P_1^2/kT \\ &= 4mc^2 (1 - P_1^2/4mkT). \end{aligned} \quad (\text{A5.12})$$

From this expression it is seen that an electron with energy $P_1^2/2m = 2kT$ keeps the same energy on the average after M collision. We shall use expression (A5.12) in Section A.6.

For high electric fields, the electron energies are higher than thermal and the loss terms predominate. Furthermore, the scattering in both cases is nearly isotropic if $M \gg m$ and the colliding particles are spheres. Hence, the analysis of kinetic theory of ionized gases can be applied to a high degree of approximation to estimate electron behaviors.

It should be stressed that several approximations are involved in this treatment. In particular it is assumed that (I) $cP_\gamma < kT$ and that (II) $P_1 \gg P_0$. If this is true, then

$$v_1/c = P_1/P_0 \gg 1 \quad (\text{A5.13})$$

so that the approximation used in considering the heavy spheres to be moving slowly holds and the mass of the heavy spheres is much greater than the electron mass:

$$M/m = (kT/c^2)/(2kT/v_1^2) = v_1^2/2c^2. \quad (\text{A5.14})$$

If conditions (I) and (II) are not satisfied, the approximations leading to (A5.5) will require revision.

³⁰ If v_{1a} is the velocity towards centers, then the probability of collision is weighted by $[1 + (v_M/v_{1a})]$ and the term linear in v_M in the energy, which is $(\frac{1}{2}m)(4v_{1a}v_M)$, contributes $2(v_M^2/m)$ to the average transfer.

A.6 APPROXIMATE TREATMENTS OF MOBILITY IN HIGH FIELDS

A correct treatment of mobility in high electric fields \vec{E} is based upon finding the steady state distribution function $f(\vec{P}, \vec{E}, T)$ which satisfies the Boltzmann equation, i.e. a function for which the rate of change due to acceleration by \vec{E} just balances that due to scattering. This method leads at once to rather formidable mathematics which may tend to obscure somewhat the physical forces at work. We shall in this section derive relationships between drift velocity and \vec{E} on the basis of simpler models and shall compare the results with the exact treatment as given in the literature for the case of a gas.

For this purpose, we shall first suppose that the field in effect raises the electrons to a temperature T_e which is greater than the temperature T of the phonon distribution. The electrons with temperature T_e will have collisions at a rate $(T_e/T)^{1/2}$ greater than before and their mobility will be reduced from its equilibrium value μ_0 to a new value μ

$$\mu = (T/T_e)^{1/2} \mu_0. \quad (\text{A6.1})$$

The average rate at which the electric field does work on an electron is then

$$(d\mathcal{E}/dt)_{\text{field}} = \text{Force} \times \text{Speed} = q\mu E^2. \quad (\text{A6.2})$$

For steady state conditions this must be equal to minus the average rate at which an electron gains energy from the phonons. Denoting this by $(d\mathcal{E}/dt)_{\text{phonons}}$ we have

$$(d\mathcal{E}/dt)_{\text{field}} + (d\mathcal{E}/dt)_{\text{phonons}} = 0. \quad (\text{A6.3})$$

In order to calculate the average rate of energy loss to the phonons, we consider the average energy gain of an electron of momentum P_1 . As given by (A5.12):

$$\langle \delta\mathcal{E} \rangle_{P_1} = 4mc^2 [1 - (mv_1^2/4kT)]. \quad (\text{A6.4})$$

According to our assumption, the number of electrons in the velocity range v to $v + dv$ is $N(v) dv = A \exp(-mv^2/2kT_e) v^2 dv$. These electrons suffer collision at a rate v/ℓ . Hence the average rate of energy gain is

$$\begin{aligned} (d\mathcal{E}/dt)_{\text{phonons}} &= \int \langle \delta\mathcal{E} \rangle_P (v/\ell) N(v) dv / \int N(v) dv \\ &= (8/\sqrt{\pi})(mc^2 v_e/\ell) [1 - (v_e/v_T)^2] \end{aligned} \quad (\text{A6.5})$$

where we have introduced

$$v_T = (2kT/m)^{1/2}, \quad v_e = (2kT_e/m)^{1/2}. \quad (\text{A6.6})$$

We see that for thermal equilibrium, with $T = T_e$ and $v = v_e$, this equation gives correctly the result that there is no net interchange of energy between electrons and phonons.

The equation for mobility for the case of phonon scattering is

$$\mu_0 = 4q\ell/3\sqrt{\pi}v_Tm. \quad (\text{A6.7})$$

This expression may be used to reduce the steady state equation:

$$\begin{aligned} 0 &= (d\mathcal{E}/dt)_{\text{field}} - (d\mathcal{E}/dt)_{\text{phonons}} \\ &= (v_T/v_e)q\mu_0E^2 + (8/\sqrt{\pi})(mc^2v_T/\ell)(v_e/v_T) [1 - (v_e/v_T)^2] \end{aligned} \quad (\text{A6.8})$$

to

$$(v_e/v_T)^4 - (v_e/v_T)^2 = (3\pi/32)(\mu_0E/c)^2. \quad (\text{A6.9})$$

This equation may be solved for v_e/v_T :

$$(v_e/v_T = \sqrt{(1/2)}(1 + [1 + (3\pi/8)(\mu_0E/c)^2]^{1/2})^{1/2} \quad (\text{A6.10})$$

The drift velocity then becomes

$$v_d = \mu E = \mu_0E \sqrt{2}/(1 + [1 + (3\pi/8)(\mu_0E/c)^2]^{1/2})^{1/2}. \quad (\text{A6.11})$$

For $E \ll c/\mu_0$, we have

$$v_d = \mu_0E. \quad (\text{A6.12})$$

For $E \gg c/\mu_0$, we have²¹

$$v_d = (32/3\pi)^{1/4} (\mu_0Ec)^{1/2} = 1.36(\mu_0Ec)^{1/2}. \quad (\text{A6.13})$$

These equations define a critical field E_c at which the two limiting cases would give the same mobility:

$$E_c = (32/3\pi)^{1/2}c/\mu_0 = 1.84c/\mu_0. \quad (\text{A6.14})$$

At this critical field, the drift velocity is less than the value on either limiting form by a factor of

$$v_d/\mu_0E_c = \sqrt{2} / [1 + 5^{1/2}]^{1/2} = 0.785. \quad (\text{A6.15})$$

This reduction in mobility corresponds to an electron temperature of

$$T_e = T/(0.785)^2 = 1.62T. \quad (\text{A6.16})$$

Expressed in terms of c the drift velocity given by the limiting forms is

$$v_e = v_d \text{ (extrapolated)} = 1.84c \quad (\text{A6.17})$$

²¹ This relationship has been published in *Bulletin of Am. Phys. Soc.*, Vol. 26, No. 1, paper 55.

and the actual drift velocity is

$$v_d(E_c) = 0.785 \times 1.84c = 1.45c. \quad (\text{A6.18})$$

If we introduce E_c into the steady state equation (A6.9), and express v_c/v_T as a mobility ratio, we obtain

$$(\mu_0/\mu)^4 - (\mu_0/\mu)^2 = (E/E_c)^2. \quad (\text{A6.19})$$

We give this equation in order to show the similarity of the Maxwellian distribution case to the cruder case considered next.

A similar treatment may be given for a hypothetical distribution of electrons such that all have the same energy ε and speed v . The effective mobility of such a distribution is²²

$$\begin{aligned} \mu &= (q\tau/m) (1 + (\frac{1}{3}) d\ell n\tau/d\ell n v) \\ &= 2q\ell/3vm = \pi^{1/2} \mu_0 v_T/2v. \end{aligned} \quad (\text{A6.20})$$

The steady state equation deduced from (A6.19) and (A6.4) is

$$(v^2/2v_T^2) [(v^2/2v_T^2) - 1] = (3\pi/64) (\mu_0 E/c)^2 \quad (\text{A6.21})$$

For high fields we find that this steady state condition gives

$$v_d = (\pi/3)^{1/4} (c\mu_0 E)^{1/2} = 1.01 (c\mu_0 E)^{1/2}, \quad (\text{A6.22})$$

a value somewhat smaller than that obtained from the Maxwellian approximation. This leads to a critical field of

$$E_c = (\pi/3)^{1/2} c/\mu_0 = 1.03 c/\mu_0 \quad (\text{A6.23})$$

at which v_d given by (A6.22) extrapolates to give the same value as $\mu_0 E$. We may use this distribution and make it give identical results with the Maxwellian distribution. If we use the steady state condition for low fields, we find $v = 2^{1/2} v_T$ and

$$\mu = \mu'_0 = \sqrt{\pi/8} \mu_0 = 0.625 \mu_0. \quad (\text{A6.24})$$

In terms of this μ'_0 , the steady state equation becomes

$$(\mu'_0/\mu)^2 [(\mu'_0/\mu)^2 - 1] = (E/E'_c)^2. \quad (\text{A6.25})$$

with

$$E'_c = (8/3)^{1/2} c/\mu'_0 = 1.63 c/\mu'_0. \quad (\text{A6.26})$$

It is evident that if we chose modified values of c' and ℓ' so as to make $\mu'_0(\ell')$ become equal to μ_0 and $E'_c(c', \ell') = E_c(c, \ell)$, then the monoenergetic

²² See *E and H in S* problem 8 page 293.

approximation will give the same results as the Maxwellian distribution. We use this procedure in the following section.

As pointed out in Section A.5, the problem treated here is closely analogous to electronic conduction in gasses. For this case, an exact treatment has been given for high fields such that the motion of the large masses M may be neglected. The drift velocity is found to be²³

$$v_d = (\frac{4}{3})^{3/4} (\pi/4)^{1/2} (m/M)^{1/4} (qE\ell/m)^{1/2} / \Gamma(\frac{3}{4}). \quad (\text{A6.27})$$

Substituting kT/c^2 for M and using (A6.7) to eliminate ℓ , we obtain

$$\begin{aligned} v_d &= (\pi^3/6)^{1/4} \Gamma(\frac{3}{4}) (\mu_0 E c)^{1/2} \\ &= 1.23 (\mu_0 E c)^{1/2}. \end{aligned} \quad (\text{A6.28})$$

This value lies intermediate between the two simple approximations considered above and leads to a critical field of

$$E_c = 1.51 c/\mu_0 \quad (\text{A6.29})$$

at a velocity of

$$v_{dc} = \mu_0 E_c = 1.51 c. \quad (\text{A6.30})$$

Since the exact case gives $v_d = \mu_0 E$ for low fields and $v_d = \mu_0 (EE_c)^{1/2}$ for large fields, it is evident that either the Maxwellian or single energy distribution will approximate it well (provided suitable choices of μ_0 or μ'_0 and E_e or E'_e are made) except for a small error near E_c .

The distribution in energy for the gas case leads to a probability of finding the electron in a range v to $v + dv$ proportional to

$$\left[\exp - \int_0^v mv dv / (kT + 3M(q\ell E/3mv)^2) \right] v^2 dv \quad (\text{A6.31})$$

For high fields this reduces to

$$[\exp - (3m/4M)(v^2 m/q\ell E)^2] v^2 dv$$

It is seen that this distribution weights the low energies less heavily than does the Maxwellian for the same average energy and thus gives a lower mobility. It weights them more heavily than does the single energy and, therefore, gives a higher mobility than it.

²³ *Druyvesteyn Physica* 10, 61 (1930). See also S. Chapman and T. G. Cowling, "The Mathematical Theory of Non-Uniform Gases," Cambridge at the University Press, 1939, page 351.

A.7 THE EFFECT OF THE OPTICAL MODES

A.7a. Introduction

The treatment presented above is based entirely upon interaction with the longitudinal acoustical modes of the crystal. Since the diamond structure has two atoms per unit cell, it is also possible to have "optical modes" in which the two atoms vibrate in opposite directions. Such modes may have long wave lengths; for example, do the same thing in each unit cell, and thus correspond to small values of \vec{P}_γ . Hence they may interact with the electron waves with $\vec{P}_\gamma \doteq \vec{P}_1$. Their frequencies correspond roughly to a wave length of about $(\frac{1}{2})$ the lattice constant in the [100] direction and hence to a frequency of about

$$(4.92 \times 10^8)(\frac{1}{2})5.6 \times 10^{-8})^{-1} (2/\pi) = 1.12 \times 10^{13} \text{ sec}^{-1} \quad (\text{A7.1})$$

The last factor of $(2/\pi)$ is a crude allowance for dispersion, which leads to a decreasing phase velocity at short wave lengths. This corresponds to an energy

$$h\nu = k \ 520^\circ K. \quad (\text{A7.2})$$

These optical phonons thus contain much more energy than the acoustical phonons; the latter having at room temperature an energy of about

$$cP_1 = 2(c/v_1)(v_1 P_1/2) = (1/10)k \ 300^\circ = k \ 30^\circ K \quad (\text{A7.3})$$

[or about $k \ 100^\circ K$ if we use the higher effective value of c discussed in Section 4]. Furthermore, the optical phonons will be only slightly excited; thus collisions with them will in general involve phonon emission so that a collision will on the average result in an energy loss of nearly $500k$. This is very large compared, for example, to the average loss of about $8 \ mc^2 \doteq k \ 12^\circ$ per collision for electrons with energies of $4kT$.

A difficulty with the optical modes is that for the approximation of spherical energy bands, which we have used in earlier parts of this paper, they should have matrix elements which vanish when $P_1 = 0$. This conclusion is reached by considering the deformation potentials corresponding to an optical displacement: this may be thought of as moving one of the face-centered cubic sublattices of the diamond structure in respect to the other. Since the initial position is one of tetrahedral symmetry, there can be no first order change in the energy \mathcal{E}_c at the bottom of the conduction band. There may be a distortion of the energy spheres for higher energies, however, and this can lead to matrix elements proportional to P_1^2 and transition probabilities proportional to P_1^4 .²⁵

²⁵ This view is in disagreement with the position stated by F. Seitz in his two papers on mobility. *Phys. Rev.* 73, 550 (1948) and 76, 1376 (1949). See for example the text between equations (14) and (15) of the latter paper.

On the other hand, if the band is degenerate and has energy surfaces consisting, for example, of three sheets, then an optical displacement may split the degeneracy and the shift in energy for $P_1 = 0$ can be linear in the displacement. (For example consider one wave function with angular dependence of the form $(\cos \theta + \sin \theta \cos \varphi + \sin \theta \sin \varphi)$ i.e. a p -type wave function with its axis along $[111]$. Its energy should certainly change for relative displacements of the two sublattices along the $[111]$ direction since positive and negative displacements are unsymmetrical in their distortion in respect to this line.)

Chiefly from evidence on magneto-resistance, the writer is convinced that the electron energy band is complex in form. Thus it would be expected that the optical modes would have matrix elements for low values of P_1 . We shall assume that this is the case but shall not endeavor to deal with a non-spherical band. This an inherently inconsistent approach, but should give at least a semiquantitative agreement with an exact theory.

In order to illustrate the effect of the optical modes, we shall assume for the moment that for high fields they are the dominant mechanism of scattering and that the scattering is isotropic. If the mean free time between collisions is τ , then the power input is

$$(d\mathcal{E}/dt)_{\text{field}} = q^2 \tau E^2 / m. \quad (\text{A7.4})$$

If the temperature is so low that the optical modes are only slightly excited, the transitions will in general absorb an optical phonon so that

$$(d\mathcal{E}/dt)_{\text{op}} = h\nu / \tau. \quad (\text{A7.5})$$

The steady state condition leads to the surprising but simple result that

$$v_d = q\tau E / m = (h\nu / m)^{1/2} \quad (\text{A7.6})$$

so that the drift velocity is independent of E .

If we insert $k\ 520^\circ K$ for $h\nu$ and the free electron mass for m , v_d becomes the velocity of an electron with $k\ 260^\circ K$ of energy giving

$$v_d = 0.88 \times 10^7 \text{ cm/sec.} \quad (\text{A7.7})$$

The limiting value on Fig. 2 for $298^\circ K$ corresponds to extrapolating Ohm's law to about 1500 volts/cm or a drift velocity of $1500 \times 3600 = 0.54 \times 10^7$. The limiting value for $77^\circ K$ is about twice as high. These values are seen to be in reasonable agreement with the predicted value.

It should be pointed out, however, that the answer obtained for v_d depends implicitly on the assumption that a relaxation time may be used in the simple way employed above. To illustrate that the result is not completely general we refer the reader to equation (4.4) which was obtained

on the basis of a somewhat different treatment. According to (4.4)

$$\begin{aligned} v_d &= (\tfrac{1}{2}) (2h\nu/m)^{1/2} = (h\nu/2m)^{1/2} \\ &= 0.63 \times 10^7 \text{ cm/sec.} \end{aligned} \quad (\text{A7.8})$$

a result smaller than (A7.6) by a factor of $2^{1/2}$.

A correct treatment of the optical modes together with acoustical modes would involve solving the Boltzmann equation to find the steady state distribution. This will obviously present problems of considerable complexity. In particular scattering will suddenly begin to increase when the electron acquires an energy, $\epsilon_1 > h\nu$ and it seems unlikely that analytic solutions can be obtained. Even the Maxwellian distribution leads to somewhat complicated integrals.

A.7b. Estimate of the Matrix Element

In order to proceed further we must estimate the order of magnitude of the optical scattering matrix element. For this purpose we introduce a "deformation potential" coefficient for the optical modes by the equation

$$\epsilon_{2n} = \partial \epsilon_c / \partial (x/x_0) \quad (\text{A7.9})$$

where x is the displacement parallel to the x -axis of one sublattice in respect to the other and x_0 is the x -component of relative displacement of the sublattices for equilibrium conditions. The same reasoning as used in treating mobility by deformation potentials²⁶ may then be applied and the matrix element evaluated by analogy with the dilatation waves. For the latter the matrix element may be written in the form

$$|U_\Delta|^2 = \epsilon_{1n}^2 \langle \Delta^2 \rangle / 2 \quad (\text{A7.10})$$

where Δ is the dilatation and $\langle \Delta^2 \rangle$ is the average (dilatation)² for the mode before and after transition.²⁷ Since half the energy in a running wave is potential

$$\begin{aligned} \tfrac{1}{2} c_{tt} \langle \Delta^2 \rangle V &= \tfrac{1}{2} h\nu \times [\text{average of } (n + \tfrac{1}{2})] \\ &= h\nu (2n + 1 + \delta n) / 4. \end{aligned} \quad (\text{A7.11})$$

This leads to the form introduced in equation (A4.1). By analogy, for the optical modes we should take

$$|U_{op}|^2 = \epsilon_{2n}^2 \langle (x/x_0)^2 \rangle / 2 \quad (\text{A7.12})$$

²⁶ W. Shockley and J. Bardeen, *Phys. Rev.* 77, 407-408 (1950) and J. Bardeen and W. Shockley, *Phys. Rev.* 80, 72 (1950).

²⁷ See *E and H in S*, page 528.

where the stored energy for deformation (x/x_0) is

$$\frac{1}{2} c_{00} (x/x_0)^2 V \quad (\text{A7.13})$$

and the average value for a transition from $n = 0$ to $n = 1$ is $h\nu$ for the total energy and $(\frac{1}{2})h\nu$ for potential. This leads to

$$|U_{0p}|^2 = \varepsilon_{2n}^2 h\nu / 2c_{00} V \quad (\text{A7.14})$$

As a first approximation we may take the stiffness between the planes of atoms separated by x_0 as the same as the macroscopic value. This leads to

$$c_{00} = c_{\ell\ell} \quad (\text{A7.15})$$

Furthermore, equal relative displacements of neighbors are produced by equal values of Δ and x/x_0 . Hence approximately equal changes in energy may occur so that we may assume that

$$\varepsilon_{2n} \doteq \varepsilon_{1n}. \quad (\text{A7.16})$$

Under these conditions

$$|U_{0p}|^2 \doteq (h\nu/kT) |U_{\Delta}|^2. \quad (\text{A7.17})$$

Since the energy of the optical modes is a maximum for $P_\gamma = 0$, it will change only a small fraction for values of P_γ comparable to P_1 .²³ (See Fig. 3.) Consequently, conservation of energy leads to transitions between \vec{P}_1 and a sphere with $P_2 = [2m(\varepsilon_1 - h\nu)]^{1/2}$. The probability is equal to each point on the sphere and the transition probability is readily found²⁹ to be

$$1/\tau_{0p} = (V |U_{0p}|^2 m^2 / \pi \hbar^4) v_2 \quad (\text{A7.18})$$

where $v_2 = P_2/m$ is the speed *after collision*. If we assume relationship (A7.17) between matrix elements and introduce ℓ as defined in (A4.3), then

$$1/\tau_{0p} = (h\nu/kT) v_2 / \ell \equiv v_2 / \ell_{0p} \quad (\text{A7.19})$$

where ℓ_{0p} is a sort of mean free path for optical scattering.

The dependence of v_2 upon the velocity before collision v_1 is obtained as follows:

$$\varepsilon_2 = \varepsilon_1 - h\nu \quad (\text{A7.20})$$

$$\begin{aligned} v_2 &= [2(\varepsilon_1 - h\nu)/m]^{1/2} \\ &= (v_1^2 - v_p^2)^{1/2} \end{aligned} \quad (\text{A7.21})$$

²³ See F. Seitz, "Modern Theory of Solids," McGraw-Hill Book Co., 1940, p. 122.

²⁹ See *E and H in S* of A.2, p. 493, for a similar treatment.

where v_ν is the velocity corresponding to $h\nu$:

$$v_\nu = (2h\nu/m)^{1/2}. \quad (\text{A7.22})$$

The rate of energy loss to the optical modes is simply

$$h\nu v_2/\ell_{\text{op}}. \quad (\text{A7.23})$$

A.7c. Approximate Steady State Treatment

In order to test whether or not the role of optical modes can explain Ryder's data, we shall use a very crude method. We shall assume that the electrons all have the same energy and shall calculate their mobility on the basis of the mean free time at that energy; from this we calculate the power input. We shall also calculate the power loss in the same way. It is obvious that this treatment is a very poor approximation to the actual situation. An electron which loses energy to the optical modes will, under most circumstances, have only a small fraction of its energy left afterwards; thus to assume a monoenergetic distribution is unrealistic. However, the treatment does bring into the analytic expressions the principal mechanisms and, as we shall show, appears to account for the main experimental features.

The collision frequency or relaxation time for transitions involving the optical modes is given in (A7.19) and the energy loss in (A7.23). We must introduce corresponding expressions for the effect of the acoustical modes. Since the single energy distribution is to be used over the entire range of electric fields, we must introduce some approximations like those discussed in connection with (A6.25) in order to make it converge on the correct behavior at $E = 0$. The particular choice selected is a compromise between the energy loss formulae for the Maxwellian and single energy distributions:

$$(d\mathcal{E}/dt)_{\text{acous. phonons}} = (4 mc^2 v_1/\ell)[1 - (v_1/v_T)^2]. \quad (\text{A7.24})$$

A simplified expression is also used for the mobility:

$$\mu = q\ell/mv_1 = \mu_0 v_T/v. \quad (\text{A7.25})$$

The relationship between μ_0 and ℓ given by this differs by 25 per cent from the correct relationship (A6.7); since μ_0 is an adjustable parameter in the comparison between theory and experiment, (A7.25) does not introduce any error at low fields. Equations (A7.24) and (A7.25) cause μ to converge on μ_0 and \mathcal{E}_1 on kT as E approaches zero. (It is probable that a slightly better fit to the data would be obtained by using the procedure described with equation (A6.25); the calculations based on (A7.24) and (A7.25) were made before the (A6.25) procedure was worked out, however, and it was not considered worth while to rework them for this article.)

Rewriting the equation for mobility in terms of the collision frequencies $1/\tau = v_1/\ell$ and $1/\tau_{op}$, the power input from the electric field is

$$\begin{aligned}(d\mathcal{E}/dt)_{\text{field}} &= q\mu E^2 = q^2 E^2/m [(1/\tau) + (1/\tau_{op})] \\ &= q\mu_0 E^2/(v_1/v_T) [1 + (\ell/\ell_{op})(v_2/v_1)]\end{aligned}\quad (\text{A7.26})$$

where the v_2 term is omitted if $v_1 < v_p$. The power delivered by phonons is

$$\begin{aligned}(d\mathcal{E}/dt)_{\text{phonons}} &= 4mc^2 (v_1/\ell) [1 - (v_1/v_T)^2] - h\nu v_2/\ell_{op} \\ &= (4qc^2/\mu_0)(v_1/v_T) \\ &\quad \times [1 - (v_1/v_T)^2 - (h\nu/4mc^2)(\ell/\ell_{op})(v_2/v_1)].\end{aligned}\quad (\text{A7.27})$$

The two coefficients of (v_2/v_1) are both larger than unity according to the analysis given above. We shall introduce the symbols A and B for them: Accordingly

$$A = \ell/\ell_{op} = h\nu/kT, \quad (\text{A7.28})$$

the last equality following from (A7.19), and

$$B = h\nu/4mc^2. \quad (\text{A7.29})$$

If we take $h\nu = k 520^\circ K$, m = the electron mass and $c = 5 \times 10^6$ cm/sec, we find

$$B = 87. \quad (\text{A7.30})$$

As discussed in the text, the losses appear to be larger than can be accounted for by these values of m and c . The critical drift velocity used in the fit of Fig. 4 was 2.6×10^6 cm/sec and this corresponds to a value of c of

$$c = v_c/1.51 = 1.72 \times 10^6 \text{ cm/sec} \quad (\text{A7.31})$$

according to the exact treatment based on the sphere model. (As stated in the text this means an effectiveness of energy interchange about $(1.72 \times 10^6/5 \times 10^5)^2 \doteq 10$ times larger than the simple theory.)

Our simplified energy loss equation (A7.27) leads to

$$v_c = 2c \quad (\text{A7.32})$$

so that we shall take

$$c = 1.3 \times 10^6 \quad (\text{A7.33})$$

in this section so as to agree with the critical velocities observed in Fig. 2. This leads to a value for B of

$$\begin{aligned} B &= k 520^\circ K / 4m (1.3 \times 10^6)^2 \\ &= 12.8 \end{aligned} \quad (\text{A7.34})$$

For A we shall take

$$A = 520/T \quad (\text{A7.35})$$

The only other adjustable parameter is μ_0 . For this we shall use the value based on Haynes' drift mobility and acoustical scattering.

$$\begin{aligned} \mu_0(T) &= \mu_0 (298^\circ K) (298^\circ K / T)^{3/2} \\ &= 3600 (298^\circ K / T)^{3/2} \end{aligned} \quad (\text{A7.36})$$

This value automatically fits the room temperature data in the Ohm's law range. The $T^{-3/2}$ dependence then extrapolates it to the other ranges.

The steady state condition may then be written in the form

$$x^2(1 + Ay)(AB y + Ax^2 - 1) = z^2 \quad (\text{A7.37})$$

where

$$v_p = (2\hbar v / m)^{1/2} \quad (\text{A7.38})$$

$$x = v_1 / v_p, y = v_2 / v_1 = (1 - x^2)^{1/2} \quad (\text{A7.39})$$

$$A = \hbar v / kT = (v_p / v_T)^2 \quad (\text{A7.40})$$

$$B = 12.8 \quad (\text{A7.41})$$

$$z = \mu_0 (T) E / 2cA^{1/2}. \quad (\text{A7.42})$$

This form lends itself to calculation of z as a function of x . The drift velocity is then found to be given by

$$\begin{aligned} u &= v_d / 2c = z / x (1 + Ay) \\ &= [(AB y + Ax^2 - 1) / (1 + Ay)]^{1/2} \end{aligned} \quad (\text{A7.43})$$

If $A \gg 1$, there are three distinct ranges of behavior for u versus z :

Range (I) $u \doteq z / A^{1/2}$

For $z \rightarrow 0$, $x^2 \rightarrow 1/A$, $y = 0$ and consequently,

$$u = zA^{1/2} = v_d / 2c = \mu_0 E / 2c \quad (\text{A7.44})$$

so that the low field relationship

$$v_d = \mu_0 E \quad (\text{A7.45})$$

is correctly given.

Range II, $Ax^2 \gg 1$ and $x < 1$

In this range the electrons are at high temperature but not high enough to excite the optical modes. For it

$$z^2 = Ax^4, \quad x = z^{1/2}/A^{1/4} \quad (\text{A7.46})$$

$$u = z^{1/2}A^{1/4} \quad \text{or} \quad v_d = (2c\mu_0 E)^{1/2}. \quad (\text{A7.47})$$

This corresponds to the square root range with a critical field of $E_c = 2c/\mu_0$ and $v_c = 2c$.

Range III, $x > 1$

When x is greater than unity, the optical modes enter the picture. For the three cases considered the values of A and AB are:

$$\begin{aligned} 77^\circ K, \quad A &= 6.75, & AB &= 87, \\ 193^\circ K, \quad A &= 2.69, & AB &= 34.5, \\ 296^\circ K, \quad A &= 1.74, & AB &= 22.3. \end{aligned} \quad (\text{A7.48})$$

The large value of AB means that as soon as y is appreciably greater than zero, say 0.5 corresponding to $x = 1.15$, energy losses to optical modes dominate. As y approaches unity, the value of u is approximately

$$\begin{aligned} u &\doteq [AB/(1+A)]^{1/2} \\ &= (h\nu/4mc^2)^{1/2}/(1+A^{-1})^{1/2} \end{aligned} \quad (\text{A7.49})$$

leading to

$$\begin{aligned} v_d(A, B) &= (h\nu/m)^{1/2}/(1+A^{-1})^{1/2} \\ &= v_\nu/[2(1+A^{-1})]^{1/2}. \end{aligned} \quad (\text{A7.50})$$

For the values of A and B given above, the ranges are not completely separated. In Fig. A2 we show the theoretical curves used in Fig. 5, together with the limiting lines just discussed.

For the middle or 193°K curve, we also show the fit that would be obtained if $c = 5 \times 10^5$ cm/sec, corresponding to $B = 87$ as for (A7.30). It is seen that this deviates much more from the data than does the curve based

on $c = 1.3 \times 10^6$ corresponding to $B = 12.8$. The deviation between theory and experiment would be still worse at 77°K , for which temperature the curve of Figure A2 fits the data well, as is shown in Figure 5.

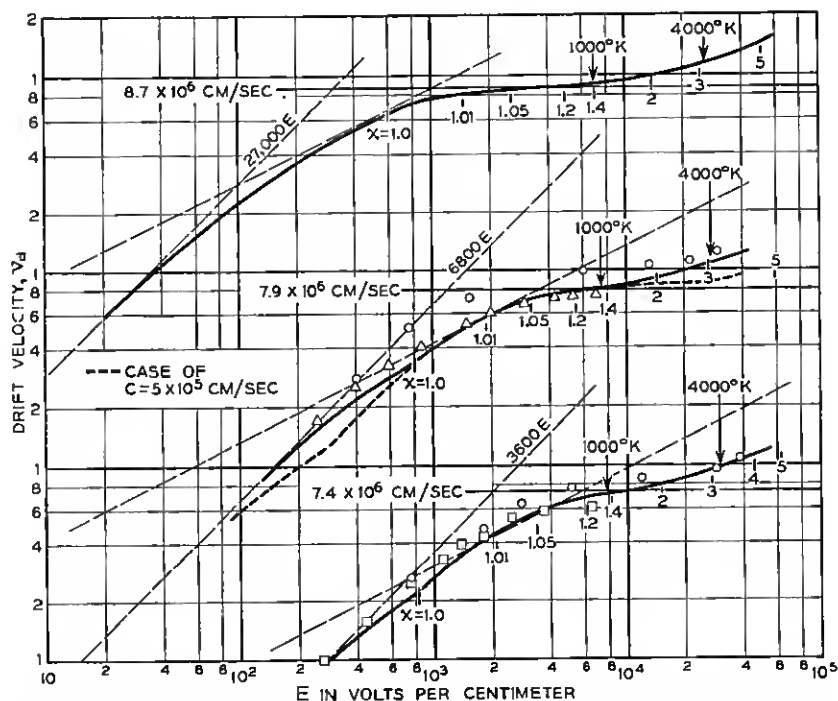


Fig. A2—The theoretical curves and their limiting forms. Some of the data from Fig. 2 are repeated here and some additional data from the original publication (Ryder and Shockley loc. cit.) are shown by crosses. A scale of values of x and of approximate "temperatures" is also shown. The dashed curve for $T = 193^\circ\text{K}$ is drawn for the case of the simple theory with $c \doteq 5 \times 10^5$ cm/sec; the change at 77°K would be even more marked.

Above range III, the Ax^2 term makes an appreciable contribution. When Ax^2 becomes large compared to B , the approximation of taking the acoustical modes to be fully excited becomes questionable. This effect may be estimated by comparing kT and the energy in an acoustical transition. The ratio is approximately

$$\begin{aligned} \frac{P_1 c}{kT} &= \frac{m v v_s c}{kT} = \frac{h \nu}{kT} \cdot \frac{2c}{v_s} \cdot x \\ &\doteq \frac{520}{300} \cdot \frac{2 \cdot 1.3 \cdot 10^6}{1.26 \cdot 10^7} x \doteq x/3. \end{aligned} \quad (\text{A7.51})$$

On Fig. A2 we show the values of x . Equ. (A7.51) leads to values of $x < 3$ for $298^\circ K$ and $x < 2$ for $193^\circ K$. Although the approximation of $h\nu$ (acoustical) $< kT$ breaks down, extrapolating the acoustical scattering into the higher range involves some compensating effects.

The effective "temperature" T_e of the electrons may be taken on the basis of this approximate treatment to be proportional to v_1^2 . In order to make T_e become equal to T for zero field, we define T_e by the equation

$$\begin{aligned} T_e &= T v_1^2 / v_T^2 = x^2 h\nu / k \\ &= 520 x^2. \end{aligned} \tag{A7.52}$$

Some temperatures deduced from this equation are also shown on Fig. A2.

Some of the data of Fig. 2 are also repeated in Fig. A2. In addition some earlier data³⁰ are also shown. These data extend to a somewhat higher range and appear to show the upward tendency predicted by the theory. The scale of temperatures indicates that for the extreme conditions experienced electron "temperatures" of about $4000^\circ K$ have been produced.

³⁰ E. J. Ryder and W. Shockley, *Phys. Rev.* 81, 139 (1950).